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CORRECTION.

In the article "Rapid Estimation of Chromium in Chrome Liquor by Use of the Immersion Refractometer," p. 665, second line from the bottom, 52.7 g. of $Cr(OH)SO_4$ should read 527 g. of $Cr(OH)SO_4$.

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THE DETERMINATION OF HYDROCHLORIC ACID AND NEUTRAL CHLORIDES IN LEATHER.*

By Arthur W. Thomas and Alexander Frieden.

A method for the determination of sulphuric acid and neutral sulphates in leather has been offered by one of us.[2] Briefly, this method is carried out as follows:

One gram of leather is placed in a 250 cc. volumetric flask and covered with 200 cc. of a 0.1 *M* KH_2PO_4 (or NaH_2PO_4) solution. The flask is immersed in a bath of boiling water for 2 hours. It is then cooled, made up to the mark with water, shaken well, and filtered through a folded paper. The first 20 to 25 cc. of filtrate are discarded, then 200 cc. of filtrate are collected, transferred to a 600 cc. beaker, 20 cc. of molar hydrochloric acid added, heated to boiling, and sulphate determined in the usual way by precipitation with barium ion. This procedure gives total sulphate. A second sample of leather is treated in a similar manner, except for the use of water instead of phosphate solution, giving the neutral sulphate present. The difference between the two values obtained shows the amount of acid sulphate in the leather.

It was undertaken to apply the same principle to the quantitative removal from, and determination of neutral and acid chlorides in leather.

Materials.

E—Strap leather, vegetable tanned, treated with hydrochloric acid.
H—Vegetable tanned leather, treated with hydrochloric acid.
I—Vegetable tanned leather, treated with hydrochloric acid.
J—Vegetable tanned leather, treated with sodium chloride.
K—Vegetable tanned leather, treated with sodium chloride.
M—Chrome calf leather, treated with hydrochloric acid.
N—Hide powder, tanned with chromic chloride.

Leathers H, I, and M were prepared by soaking finished samples of the cut-up leathers in dilute hydrochloric acid, after which they were filtered, washed just enough to remove adhering acid solution, and dried. Leathers J and K were prepared in a similar manner, using sodium chloride instead of hydrochloric acid.

* Reprinted from *J. I. and E. C.*, 12, 1186 (1920).

[1] A. W. Thomas, this Jour., 15, 504 (1920).

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Experimental Part.

Extraction with Phosphate Solution.—Experiments were carried out to note the effect of different times of heating and of different weights of leathers on the extraction of total chlorides by the phosphate solution. The reason for trying different weights was due to the fact that in the case of sulphate extraction it was found that not more than 1 g. of leather containing more than 5 per cent. SO_3 could be used, if a quantitative removal of the sulphates was to be accomplished by use of 200 cc. of the phosphate solution.

As shown below, 2 hours was found sufficient time for the digestion and 1-g. samples not too large for quantitative results. Extraction times longer than 2 hours did not yield any more chloride than the 2-hour extraction.

Leather N Gram	Chloride, Calculated as Cl, Extracted by 0.1 M KH_2PO_4 Solution in 1 hr. Mg.	2 hrs. Mg.
0.5	—	39.6
1.0	39.5	41.1
2.0	37.3	39.8

Extraction with Water.—Since neutral sulphates are quantitatively extracted from leather by means of pure water in 2 hours at 100° C., this procedure was tried upon the samples of leather containing sodium chloride, with the following result:

Leather	Cl Found KH_2PO_4 Extraction Mg	Cl Found Water Extraction Mg.
J	17.7	17.8
K	23.7	23.6

Hence, in the case of these leathers which contained neutral chlorides only, all of the chloride was extracted with water, because, as will be shown later, these yields are identical with those obtained by phosphate extraction which removes all chlorides quantitatively.

In the sulphuric acid method it was found that while all the neutral sulphate was removed by digestion in water, a small portion (7 to 10 per cent. of the total), of the acid sulphate was hydrolyzed and extracted as well, and therefore, the effect of water on the acid chloride was investigated with the result:

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Leather	Total Acid Cl Present per Gram Mg.	Acid Cl per Gram Extracted by Water in 0.5-hr. Digestion Mg.
H	19.9	19.5
M	28.1	16.9
N	40.1	17.1

It was obvious from these experiments, that the water extraction could not be used for separation of neutral chloride from acid chloride in leather. Sample H showed practically complete removal of the hydrochloric acid by water. This effect has been noted by us in other samples of vegetable tanned leathers which had been treated with hydrochloric acid, and we do not consider such prepared samples as proper material upon which to base a test. It appears that all of the hydrochloric acid does not combine chemically with finished vegetable tanned leathers, because it reacts with the same groups of the collagen molecule as tannins do. In the cases of chrome tanned samples, M and N, all the acid chloride was not extracted by water, but since the amount removed was so large, it was evident that the method which worked very well for sulphuric acid and neutral sulphate separation would have to be modified if separation of acid and neutral chloride was to be attained.

Since, in our opinion, acids are chemically combined with collagen, provided they come in contact with the collagen before all the reactive groups of the collagen are combined with tanning agents, the removal of an acid from leather by means of hot water is due to hydrolysis. It is evident then that collagen hydrochloride is much more readily hydrolyzed than collagen sulphate.

Extraction with Alcohol.—Since hydrolysis of the collagen-acid compound cannot take place in alcohol, while chlorides are soluble in this solvent, its efficacy for extraction of neutral chloride was studied. The 95 per cent. ethyl alcohol was purified by distillation over alkali. The typical figures given below show that alcohol quantitatively removes neutral chloride from leather. The digestion was carried out at 75° C. for 2 hours, although in many cases 1.5 hours were found to be sufficient.

Leather	Neutral Cl present per gram sample Mg	Cl extracted by alcohol per gram sample Mg.
J	17.8	17.9
K	23.7	23.6

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The amounts of acid chloride extracted by alcohol after 2 hours digestion at 75° C. were as follows:

Leather	Acid Cl[1] present per gram sample Mg	Acid Cl[1] extracted by alcohol per gram sample Mg
I	21.1	5.4
L	28.1	5.4
N	40.1	5.9

[1] While we call this "acid chloride," we have no means of knowing whether all is present as such. The leathers in the cases of I and L, and the hide substance in the case of N were treated with acid chloride solutions, but this treatment does not necessarily result in its all existing in the leather as acid chloride, since it is quite possible that some may have been converted to neutral chloride in the leather.

The above experiments indicated that while neutral chloride was quantitatively extracted by alcohol, a small amount of the acid chloride present was apparently extracted as well, but on account of the possibility that some of the chloride considered as acid chloride might have been converted to neutral chloride, and also since no method for the determination of hydrochloric acid in leather is available, we feel justified in offering this as a satisfactory method at the present time.

METHOD.

Total Chloride.—One gram of leather is placed in a 250 cc. volumetric flask and covered with 200 cc. of a 0.1 *M* solution of KH_2PO_4 or NaH_2PO_4. The flask is immersed in a bath of boiling water for 2 hours, and shaken occasionally. The solution is then cooled, made up to the mark with water, shaken well, and filtered through a folded paper. The first 20 to 25 cc. of filtrate are discarded, then 200 cc. of the filtrate are collected in a volumetric flask, transferred to a 600 cc. beaker, and acidified by addition of 10 cc. of molar nitric acid which prevents precipitation of silver phosphate when the silver nitrate is added later. The solution is heated and 10 cc. of 0.1 *M* silver nitrate solution added. After the silver nitrate treatment, a further addition of 20 cc. of concentrated nitric acid (15 *M*) is made, and this mixture is evaporated in the dark to about 50 cc. volume, in order to oxidize and dissolve organic matter which has precipitated with and contaminated the silver chloride. The solution is then diluted with about 200 cc. of water, heated, and filtered through a Gooch crucible. The silver chloride is washed, dried, and weighed in the

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usual manner, and the total chloride in the leather is computed from the weight of silver chloride obtained.

Acid Chloride.—A second sample of 1 g. of leather is covered with 200 cc. of purified 95 per cent. alcohol in a 250 cc. volumetric flask and digested at about 75° C. for 2 hours, with occasional shaking. The contents of the flask are then cooled, made up to the mark with water, mixed and filtered *immediately.* (If made up to the mark with alcohol, there is no danger of hydrolysis of the collagen-acid compound, and hence *rapid* mixing and filtration are not required.) The first 20 to 25 cc. of filtrate are discarded, and 200 cc. of filtrate collected, transferred to a 600 cc. beaker, made just alkaline with sodium hydroxide, and the alcohol evaporated off (if it is desired to recover the alcohol, a flask may be used, but after the alcohol is removed, the residue should be washed into a beaker). Sufficient nitric acid is added to render the solution slightly acid. The solution is heated and 10 cc. of 0.1 *M* silver nitrate solution added. From this point the procedure is identical with that outlined above, after the addition of silver nitrate. From the silver chloride obtained here, the neutral chloride may be calculated, and this value subtracted from the total chloride value indicates the amount of acid chloride present in the leather.

Results.

The results obtained by this method were compared with the amounts of chloride obtained by the method of determination of total chloride by ashing the leather, previously soaked with sodium carbonate solution and covered with dry sodium carbonate. The ashing was conducted in a muffle furnace at as low a heat as possible, and the amount of chloride present in the sodium carbonate was determined, and correction applied in each case.

Leather	Total Cl found by ashing per cent.	Total Cl found by phosphate digestion (1) per cent	Neutral Cl found by alcohol digestion (2) per cent	Acid Cl difference between (1) and (2) per cent
N*	4.21	4.01	0.59	3.42
M*	2.80	2.81	0.54	2.27
I*	2.16	2.11	0.54	1.57
E*	1.23	1.21	—	—
J†	—	1.79	1.78	0.01‡
K†	2.52	2.37	2.36	0.01‡

* Presumably all chloride present was acid chloride.
† All chloride present was neutral chloride.
‡ Actually zero; the method is not accurate to this extent.

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In general, the total chloride found by the method of ashing is greater than that found by the phosphate digestion. This is due to chlorine present as part of the protein molecule in the leather or in forms other than chloride.

An objection might be raised against the use of ethyl alcohol. There seems to be no reason, however, why denatured alcohol that has been twice distilled, first over phosphoric acid and then over alkali, would not serve just as well as pure ethyl alcohol.

ACKNOWLEDGMENT.

We take pleasure in acknowledging the generous support of Messrs. A. F. Gallun and Sons Company in this investigation.

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THE ANALYSIS OF SULPHONATED OILS—AN IMPROVEMENT OF THE HART METHOD.

By C. Gebhart Bumcke.

Rec'd. November 17, 1920.

A quick and reliable method for the determination of combined SO_3 in sulphonated oils is a very important matter for all those who have to deal with or use sulphonated oils. After some recent improvements—that is the addition of ether and brine to facilitate the titration of the watery layer—the Hart method seemed to offer the long looked for short method for the determination of the combined SO_3 and the total alkali. Unfortunately the values for SO_3 are almost always somewhat smaller than those obtained by the wet method with HCl (analyses a and b)[1] or by the ash method (analyses c to m). The difference between the results of the Hart Method and the other methods became still greater for oils that are highly sulphonated; that is, where the combined SO_3 is as high as 5 to 7 per cent. or more.

As there was no objection to the principle of the Hart Method, the error had to be looked for in its application. What is effected in the Hart Method, namely the splitting off of SO_3 from the sulpho-fatty acids is also accomplished in the wet method with HCl. The latter requires 25 cc. of water for the solution of the oil and an addition of at least 30 cc. of diluted HCl (1 : 5). This is equal to 55 cc. of about normal HCl solution. The Hart Method requires only 25 cc. one-half normal H_2SO_4 solution.

[1] Compare analyses given in previous reports, this JOUR., 15, 285 (1920), and 14, 270-272 (1919).

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The reason for the lower values obtained by the Hart Method appeared to be the insufficient quantity of mineral acid to hydrolyze the sulpho-fatty acids. The experiment showed that this was indeed the case. A trial was made with double the quantity of the one-half normal acid, but though the results were slightly higher (analysis i) the solution was still too great to obtain perfect decomposition, the results were still lower than those obtained by the wet method with HCl or the ash method.

The perfect decomposition of the sulpho-fatty acids is obtained only by the use of 25 cc. normal H_2SO_4 solution (50 cc. normal solution did not give any material variation of the result) and by good boiling for one hour over a Bunsen burner, the common electric hot plate does not give enough heat for the vigorous boiling that is necessary to obtain perfect decomposition. The boiling of about 10 grams of oil with 25 cc. normal H_2SO_4 solution was done in a 500 cc. Erlemmeyer flask, and the addition of several small pieces of pumice stone prevented the bumping or splashing up into the condenser.

This improvement also obviates the objections of G. F. Pickering[2] to the Hart Method. He found that the fat from the Hart process, extracted with ether and fused with sodium carbonate, still contains 0.7 to 1.0 per cent. sulphuric acid.

ORGANIC SO_3 CALCULATED FOR DRY OIL.

	a	b	c	d	e	f	g	h	i	k	l	m	n
Wet Method	4.90	4.66	—	—	—	—	—	—	6.53	—	—	—	—
Ash Method	—	—	4.71	5.06	5.96	6.52	6.84	7.01	6.68	6.80	6.52	6.12	—
Hart Method with 25 cc. N/2 H_2SO_4	4.43	4.20	4.28	4.84	5.48	6.13	6.14	6.34	5.69	5.60	5.63	5.09	5.32
Hart Method with 50 cc. N/2 H_2SO_4	—	—	—	—	—	—	—	—	5.90	—	—	—	—
Improved Hart Method with 25 cc. N. H_2SO_4	—	—	—	—	—	—	—	—	6.83	6.94	6.67	6.03	6.47

The above figures are the mean values of two determinations, most of which agreed within less than 0.10 per cent.

LABORATORY OF THE NATIONAL OIL PRODUCTS CO.,
Harrison, N. J.

[2] G. F. Pickering, The Commercial Examination of Sulphonated Oils, *J. Soc. Chem. Ind.*, 39, 305T (1920); Abst. this JOUR., 15, 630 (1920).

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THE DETERMINATION AND CONTROL OF ACIDITY IN TAN LIQUORS.*

By W. R. Atkin and F. C. Thompson.

The importance of the acidity of tan liquors is shown by the ample literature on the subject describing for the most part work which has not achieved its aim, namely, the actual measurement of the swelling power of tan liquors. At the outset we may state our opinion that acidity, even when the presence of salts of weak acids is taken into account, is not the only factor governing swelling. Two factors, the influence of which is obscure are: (*a*) the astringency and actual tanning effect of the tannins present and (*b*) the effects of neutral salts of strong acids such as sodium chloride, sodium sulphate, etc. A well conceived and direct method of arriving at the effect of astringency, etc., is that of Claflin,[1] who carries out swelling experiments with hide powder and the liquor under investigation where the amount of liquid absorbed by the hide powder measures the swelling power. The influence of neutral salts has been well brought out in numerous papers by J. A. Wilson and his collaborators,[2] A. W. Thomas and M. E. Baldwin[3] and J. W. McBain.[4] The effect of adding sodium chloride to dilute hydrochloric acid is to raise the hydrion concentration as measured by the hydrogen electrode whereas sodium sulphate added to weak acids has an opposite effect.

McBain found that the partial vapor pressure of acetic acid in dilute solution was greatly augmented in the presence of sodium chloride. These interesting effects are believed by Wilson to be intimately connected with the degree of hydration of the added ions whereas McBain speaks of "enhanced chemical potential." Whatever the cause the effect is of great importance, particularly in chrome tanning.

In this paper, however, we are concerned only with a direct determination of acidity. All previous attempts have depended

*Reprinted from *J. S. L. T. C.*, 4, 143 (1920).

[1] A. A. Claflin, This Jour., 15, 234 (1920).

[2] J. A. Wilson and E. Kern, This Jour., 12, 445 (1917); 15, (1920).

[3] A. W. Thomas and M. E. Baldwin, *J. Amer. Chem. Soc.*, 41, 1981 (1919).
M. E. Baldwin, This Jour., 14, 10 (1919).

[4] J. W. McBain, *Chem. Soc. Trans.*, 115, 1332 (1919).

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upon titration of the tan liquors with alkali. H. R. Procter and R. A. Seymour-Jones[5] published in 1910 a comprehensive review of the earlier work on this subject and in addition described several variations involving the use of indicators. The two main difficulties, however, were:

(*a*) The color of the tan liquors masked the color of the indicator.

(*b*) Except in a neutral atmosphere there was always a considerable oxidation and darkening on the addition of alkali.

Attempts have been made to overcome the first difficulty by detannization previous to titration but this procedure causes serious errors as in almost all cases there is a marked co-precipitation of acid. This objection applies to the present official method of the A. L. C. A. in which detannization is effected by means of an alcoholic solution of gelatine. Stiasny,[6] however, detannizes with a mixture of hydrochloric acid and formaldehyde and in this case there appears to be no loss of acid but the method can only be applied to catechol tans.

The question now to be discussed is what acidity should be measured. It is necessary to define at the outset what is meant by "acidity" and to show that measurement of total content in acid even if this could be accurately performed would not give the information which is desired by the sole leather tanner. A concrete example may make this point clear. Consider the two following cases: (*a*) 25 cc. of N/10 acetic acid, and (*b*) 25 cc. of N/10 acetic acid containing 0.205 g. of sodium acetate and consequently also N/10 in this substance. If these two solutions were titrated with alkali using phenolphthalein as indicator the same result would be obtained in each case, but if an attempt were made to titrate using methyl orange, it would be found that mixture (*b*) was already alkaline. In harmony with this, the swelling power on water swollen gelatine of solution (*b*) would be nil, whereas (*a*) would produce a pronounced increase of swelling. The explanation is found in a consideration of the ionization phenomena in the two cases.

[5] H. R. Procter and R. A. Seymour-Jones, *Coll.*, 1911, p. 219 *et seq.*; This Jour., **6**, 52 (1911).

[6] E. Stiasny, *Der Gerber*, 1905, p. 185.

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As is well known the property of acidity is due to the presence in solution of hydrogen ions. An acid in solution dissociates into ions according to the following scheme:

$$HAc \rightleftharpoons H^{\cdot} + Ac^{1}$$

In the case of weak acids the extent of this dissociation, *i. e.*, the concentration of ions produced is in accordance with the well known law of mass action.

This states that under given circumstances of original concentration and temperature, the concentrations of the products of reactions at equilibrium are, when multiplied together, in strict proportion to the concentrations of reacting substances also multiplied together. In other words if A and B react together to form X and Y, then at equilibrium $[A] \times [B] = K[X] \times [Y]$.

The square brackets indicate *concentrations* and K is a number termed the equilibrium constant of the reaction.

Consider from this point of view the electrolytic dissociation or ionization of a weak acid, *i. e.*, one which is only ionized to a slight extent. Here we only have *one* reacting substance, namely, the acid which is partially split up into the *two* reaction products, the kation ($H^{\cdot}$) and the anion (Ac^{1})—

$$K\,[HAc] = [H^{\cdot}] \times [Ac^{1}]$$

Here K is the dissociation or ionization constant, and in the case of weak acids is always very small, *e. g.*, 0.000018 for acetic acid. The square brackets indicate concentration in terms of normality, *i. e.*, for N/10 acetic acid, of which over 98 per cent. remains undissociated, $[HAc] = 0.1$ approximately, being actually a little less.

Whatever other ions may be present in solution at the same time as those of acetic acid, the above equation holds good. Consequently if the concentration of the anion, $[Ac^{1}]$, be increased by some means, without increasing the concentration of undissociated acid [HAc], then in order to maintain the equality, the concentration of the kation, $[H^{\cdot}]$ must diminish. In other words the acidity is diminished. In the case of decinormal acetic acid we have—

$$K\,[CH_3COOH] = [H^{\cdot}] \times [CH_3COO^{1}] = [H^{\cdot}]^{2}$$

since hydrogen and acetate ions are necessarily equal in number.

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Since the acid is decinormal and almost all undissociated, we have approximately—

$$0.1K = [H\cdot]^2$$
$$\text{or } [H\cdot] = \sqrt{0.0000018}$$
$$= 0.00134 = 1.34 \times 10^{-3}$$

The effect of adding sodium acetate is to increase largely the number of acetate ions. Usually the salt of even a weak acid is largely dissociated, and in extending the calculation to the case of mixture (*b*) we shall assume as an approximation that sodium acetate is completely ionized in decinormal solution. Thus [Ac^1] now = 0.1, whilst [HAc] is unaffected. The sodium ions produced do not affect the case. We still have—

$$K\,[CH_3COOH] = [H\cdot] \times [CH_3COO^1]$$
$$\text{but now } 0.1\ K = [H\cdot] \times 0.1$$
$$\text{or } [H\cdot] = K = .000018 = 1.8 \times 10^{-5}$$

Thus [H·], or the acidity has been reduced to less than 2 per cent. of its value in N/10 acetic acid. The effect of any other amount of sodium acetate can be calculated easily. Suppose the N/10 acid to be made N/1 in sodium acetate. Then approximately—

$$0.1\ K = [H\cdot] \times 1.0$$
$$\text{or } [H] = \frac{K}{10} \text{ or } 1.8 \times 10^{-6}$$

More accurate results can be obtained by finding the actual percentage dissociation of sodium acetate from the tables and using it in the calculation.

An interesting and important property of mixtures of weak acids and their salts is that the [H·] is very little altered by even considerable dilution. Such solutions are called "buffers" and their behavior is readily explainable in the light of the above equations. Consider again the case of mixture (*b*). We have here—

$$0.1\ K = [H\cdot] \times 0.1.$$

This formula may now be made more accurate by introducing corrections for the not quite complete ionization of the sodium acetate, which in N/10 solution is ionized to the extent of 79 per cent. and in N/100 solution to 87 per cent.

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Consequently for the N/10 solution the above equation becomes—

$$0.1 \times K = [H\cdot] \times 0.1 \times \frac{79}{100}$$

$$0.1 \times 1.8 \times 10^{-5} = [H\cdot] \times 0.079$$

$$\text{or } [H\cdot] = 2.28 \times 10^{-5}$$

Now consider the case where mixture (*b*) is diluted ten times. We now have—

$$0.01 \times K = [H.] \times 0.01 \times \frac{87}{100}$$

$$\text{or } 0.01 \times 1.8 \times 10^{-5} = [H\cdot] \times 0.0087$$

$$\text{or } [H\cdot] = 2.07 \times 10^{-5}$$

In the case of pure acetic acid containing no added sodium acetate the [H·] is 1.3×10^{-3} in N/10 solution and 0.42×10^{-3} in N/100 solution representing a drop of nearly 70 per cent. as compared with about 10 per cent. in the case of mixture (*b*).

Now consider the case of pure distilled water which is very slightly ionized into hydrions and hydroxyl ions so that—

$$K\,[H_2O] = [H\cdot] \times [OH^1] \text{ and } [H\cdot] = [OH^1]$$

As the mass of undissociated water is very large compared with the mass of the free ions we might regard it as also constant so $[H\cdot] \times [OH^1] = Kw$.

Where Kw is the dissociation constant for pure water and has the very low value at 21° C. of 10^{-14} and thus the value for [H·] or [OH^1] is 10^{-7} gram ions per liter.

If an acid be added to distilled water, the acid is dissociated either partially or wholly, into hydrions and the anions of the acid employed. Thus [H·] in such a mixture is greater than 10^{-7} and the solution is "acid." Suppose acid had been added so that [H·] was 10^{-3} then [OH^1] would be 10^{-11} for—

$$[H\cdot] \times [OH^1] = 10^{-14}$$

From the above it will be understood that a solution is "neutral," "acid" or "alkaline" according to whether [H·] has a value equal to, greater than or less than 10^{-7} respectively. Obviously if [H·] does not equal 10^{-7}, then it cannot be equal to [OH^1].

Sörensen,[7] in order to facilitate the plotting of curves, has introduced the symbol P_H to denote what he calls the "hydrogen

[7] S. P. L. Sörensen, *Comptes-Rendus du Lab. de Carlsberg,* VIII; This Jour., 6, 128, 193 and 259 (1911).

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ion exponent," where P_H is the logarithm to the base 10 of $[H^+]$ but with the negative sign omitted or $P_H = -\log_{10}[H^+]$. For example: N/10 acetic acid has $[H^+] = 1.36 \times 10^{-3} = 10^{0.133} \times 10^{-3} = 10^{-2.867}$ so $P_H = 2.867$.

It should be noticed that P_H decreases with increasing acidity and that if $[H^+]$ be increased tenfold the value of P_H is decreased by 1.0.

From the case of acetic acid and sodium acetate mentioned above it will be seen that P_H cannot be determined by ordinary titration.

The most accurate method of determining the $[H^+]$ or P_H is by means of the hydrogen electrode and this method has been applied by Wood, Sand and Law in the case of tan liquors. The method is an electrical one, requiring a considerable amount of apparatus and does not seem to have become universally popular with tannery chemists.

Other methods depend upon the measurement of the velocity of chemical reactions such as the hydrolysis of can sugar or methyl acetate where acids are used as catalysts but these involve too much time. The simplest method is by the use of indicators and may be called the colorimetric method. It has the great advantage that it is rapid and does not require any elaborate apparatus.

As is well known indicators are substances that vary in color with varying acidity or alkalinity of the solution to which they are added. This change of color takes place over a definite range of P_H and at various points within this range the indicator shows indeterminate tints. The solution is "neutral" to the indicator at the mid point of the range. This neutrality does not mean that $[H^+] = [OH^1]$ as in pure water. For example, "neutrality" to phenolphthalein occurs about $P_H = 9$ whilst in the case of methyl orange "neutrality" is in the region $P_H = 4$, the $[H^+]$ in the latter case being 100,000 times greater than in the case of phenolphthalein. Litmus, however, has its "neutral" point at about 6.6 and brom-thymol blue at about 6.8. Table I shows a list of convenient indicators—many of which are of the new sulphone phthalein type described by Mansfield Clark, Lubs and Acree.[8] One of

[8] W. Mansfield Clark and H. A. Lubs, *J. Bact.*, **2**, 1, 109 and 191 (1917). S. F. Acree, *J. Amer. Chem. Soc.*, **41**, 1190 (1919), and previous articles.

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them, thymol blue, it will be noticed, has a double change, one in fairly strong acid solution and the other like that of phenolphthalein.

TABLE I.

Indicator	Chemical Name	Range of PH	Colour change acid-alkaline	Strength o solution
Methyl violet		0.1– 3.2	green-blue	0.02 %
Thymol blue	Thymol sulphone phthalein	1.2– 2.8	red yellow	0,04 %
Brom-phenol-blue. . .	Tetra-brom-phenol sulphone phthalein	2.8– 4.6	yellow-blue	0.04 %
Methyl orange	p-Dimethyl amino azobenzene sulphonic acid	3.1– 4.4	red-yellow	0.01 %
Methyl red	p-Dimethylamino azobenzene o-carboxylic acid	4.4– 6.0	red-yellow	0.02 % in 60 % alcohol.
Brom-cresol-purple . .	dibrom-o-cresol sulphone phthalein	5.2– 6.8	yellow-purple	0.04 %
Brom-thymol-blue . .	dibrom-thymol sulphone phthalein	6.0– 7.6	yellow-blue	0.04 %
Phenol red	phenol sulphone phthalein	6.8– 8.4	yellow-red	0.02 %
Cresol red	o-cresol sulphone phthalein	7.2– 8.8	yellow-red	0.02 %
Thymol blue	thymol sulphone phthalien	8.0– 9.6	yellow-blue	0.04 %
Phenolphthalein . . .		8.3– 10.0	colourless-red	0.05 % in 50 % alcohol.

The colorimetric method has been described by various workers, including Veley and Sörensen, but the results obtain were only rough in the case of colored fluids. Sörensen also pointed out that the presence of proteins vitiated the results with certain indicators. This was especially the case with colloid indicators such as congo-red. Walpole surmounted the difficulties due to the color of the fluids by matching the solution under investigation (which contained the indicator) against a colorless solution of standard P_H containing the same amount of indicator observed through a layer of the colored fluid. His method was modified by Hurwitz, Meyer, and Osterberg,[9] who used test tubes held in a box, and finally by Cole and Onslow[10] who have further improved this latter device, which is termed a "comparator" by the addition of a ground glass plate as shown in the diagram:

[9] Hurwitz, Meyer and Osterberg, *Johns Hopkins Hospital Bulletin*, 27, 16 (1916).

[10] Cole and Onslow, *Practical Physiological Chemistry*, by S. W. Cole (published by Heffer, Cambridge).

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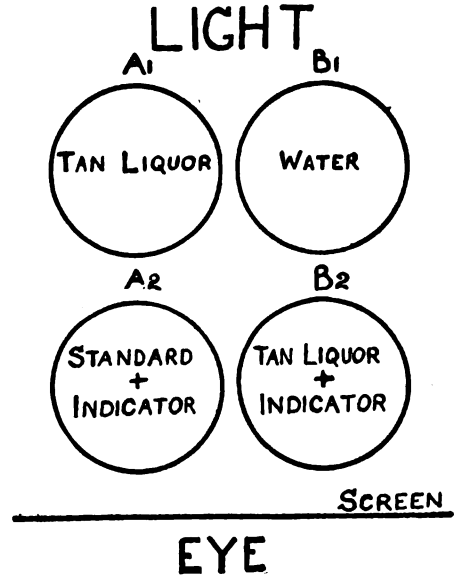

For determining the acidity of tan liquors a comparator which takes two pairs of tubes is as large as is necessary. The method of procedure is as follows:

Test-tube A_1 contains 10 cc. of filtered tan liquor, A_2 contains 10 cc. of a solution of standard P_H together with five or ten drops of a suitable indicator, *i. e.*, an indicator which is changing its shade distinctly in that region of acidity. Test tube B_1 contains distilled water, and B_2 10 cc. of filtered tan-liquor and the same number of drops of indicator solution as in A_2. If on looking through the two pairs of tubes, the colors match, then the P_H of the tan-liquor is that of the standard used in A_2. If not, other standards of deeper or lighter shade as may be required are substituted for that in A_2. The matching is usually performed in a minute or so provided that the necessary ranges of standards are to hand. The test tubes must be of colorless glass and of the same diameter. A selection can easily be made by pipetting 10 cc. of water into a number of, say, 5/8-in. tubes, which are very convenient, and using those which give the same level of water. The tubes are best divided thus into sets, marked, and kept separately in boxes. The most convenient means of obtaining drops of indicator solution of equal size, is to use the slow dropping Dreyer pipettes which have a capillary end about 1 in. long. With

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these pipettes there is no danger of adding too many drops accidentally. As a source of light a Nernst lamp proved to be excellent, and good results were obtained with an inverted incandescent gas mantle and with an electric lamp of the half-watt type.

Tan liquors have acidities which lie as a rule between $P_H = 3.0$ and $P_H = 4.5$. Exceptions are often found in the case of synthetic tannins which may be so acid as to reach $P_H = 1.5$. It must first be emphasized that neutrality from the tanner's point of view is the point of minimum swelling and that this is *not* when $P_H = 7$, *i. e.*, when $[H\cdot] = [OH^1]$. Experiments by Procter, Loeb, Michaelis and by the authors all tend to fix the iso-electric point of gelatin or the point of minimum swelling at $P_H = 4.5-4.7$.

The determination of the point of minimum swelling gives us one limit for the range of P in the acid standards, It is plainly not necessary to go nearer to neutrality than $P_H = 4.7$, The other limit may be taken as $P_H = 2.8$ for most purposes. Only synthetic or treated tannins are likely to lie outside this range. The standards used were mixtures of (1) acetic acid and sodium acetate, (2) acid potassium phthalate and hydrochloric acid. The best indicator appears to be tetra-brom-phenol-sulphonephthalein or brom-phenol-blue. The color of this indicator changes continuously from $P_H = 2.8$ to $P_H = 4.6$, though not very much near the limits. Brom-phenol-blue, however, is dichroic and is best observed through a yellow color-screen which cuts off blue rays. A convenient mode of making such a screen is to paint transparent parchment with a mixture of 0.6 per cent. solution of phenol red and M/5 solution of potassium dihydrogen phosphate (27.23 grams/liter). The preparation of the standards is a very simple matter, following the tables given. The solutions required are N/5 acetic acid, N/5 sodium acetate prepared by neutralizing 200 cc. N/1 caustic soda with N/1 acetic acid and diluting to one liter, M/5 acid potassium phthalate (40.828 grams/liter), N/5 caustic soda, and N/5 hydrochloric acid.

TABLES.

SERIES I.—50 cc. M/5 acid potassium phthalate; x cc. N/5 HCl, mixed and diluted to 200 cc.

PH.	x.	PH.	x.	PH.	x.
2.8	26.42	3.2	14.70	3.6	5.97
2.9	22.80	3.3	11.80	3.7	4.30
3.0	20.32	3.4	9.90	3.8	2.63
3.1	17.70	3.5	7.50	3.9	1.00

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SERIES II.—50 cc. M/5 acid potassium phthalate; x cc. N/5 NaOH, mixed and diluted to 200 cc.

PH.	x.	PH.	x.
4.0	0.40	4.3	5.17
4.1	2.20	4.4	7.50
4.2	3.70	4.5	9.60
		4.6	12.15

SERIES III.—x cc. N/5 sodium acetate + 100 — x cc. N/5 acetic acid.

PH.	x.	100-x.	PH.	x.	100-x.
3.8	12	88	4.3	31	69
3.9	15	85	4.4	37	63
4.0	18	82	4.5	42.5	57.5
4.1	22	78	4.6	48	52
4.2	26.5	73.5	4.7	54	46

For instance a solution of $P_H = 3.8$ may be prepared in either of the two following ways: (*a*) 50 cc. M/5 phthalate + 2.63 cc. N/5 hydrochloric acid, diluted to 200 cc., or (*b*) 12 cc. N/5 sodium acetate + 88 cc. N/5 acetic acid, 10 cc. of either of these solutions, together with five drops of brom-phenol-blue solution is pipetted into a test tube, corked well and labelled $P_H = 3.8$. It will be found convenient when working in the range from $P_H = 2.8$ to $P_H = 3.7$ to use 10 drops of indicator solution in order to intensify the color differences. The whole range required should be made up and kept in a test tube stand, preferably in the dark. The authors have found that the colors do not change appreciably in the course of a month. These sets of standards have been worked out by Clark and Lubs and have been standardized against the hydrogen electrode.

A number of tannin solutions have been examined both in the above way and by Procter's lime-water method, with the following results, which have been arranged in order of increasing acidity:

Tan liquor	Proctor lime water method cc satd. lime water per 10 cc. tan liquor	Colorimetric method PH.	Colorimetric method [H·] as normality
No. 1	1.8	4.3	5×10^{-5}
No. 2	5.6	4.2	6.3×10^{-5}
No. 3	6.2	4.1	8×10^{-5}
No. 4	6.8	4.1	8×10^{-5}
No. 5	16.2	3.8	1.6×10^{-4}
No. 6	17.3	3.7	2×10^{-4}
No. 7	27.9	3.4	4×10^{-4}
No. 8	34.5	3.1	8×10^{-4}

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It will be noticed that the lime water figures are in the same order as the acidities, though no exact correspondence is revealed. There is no necessary connection between P and the lime-water figure, however.

If it be required to raise the acidity of a tan liquor this can easily be done by titrating the liquor with a standard solution of the acid to be used until its acidity reaches the required P_H as shown in the comparator; a calculation will then show how much commercial acid should be added to the liquor in the pit. What, however, is a desirable P_H must be fixed by the tanner according to the class of leather he is dealing with. The best way is to note carefully the acidities of liquors which he finds satisfactory, and to reproduce these as required. It will be obvious that acid is titrated by acid; no alkali is used, and the difficulties due to oxidation and darkening entirely disappear.

An interesting application of this acidity method is in the case of freshly made analytical solutions of tannin. A surprising variation in acidity was found, the range being as great as in used liquors.

Tanning materials	Range of PH.
Solid mimosa extract (4 samples)	4.1–4.3
Sumach (4 samples)	4.1–4.2
Liquid myrobalan extract (3 samples)	3.3–3.4
Solid quebracho extract (2 samples)	4.1
Liquid quebracho extract (3 samples)	4.0–4.2
Solid chestnut extract (1 sample)	3.5
Liquid chestnut extract (2 samples)	3.7–3.75

Wood, Sand and Law[11] have previously determined the acidity of tan liquors directly by the hydrogen electrode, which is the standard method and much more accurate than the method described in this paper. However, it has not become popular with tannery chemists and our purpose is to give a method, which whilst sufficiently accurate, is yet simple in execution and easy to understand. The electrometric method is no doubt easily and quickly carried out when the complicated apparatus is once set up, but to understand and appreciate the method of working requires a considerable acquaintance with difficult thermodynamic theory.

[11] Wood, Sand and Law, *Coll.*, 1911, pp. 150 and 432; This Jour., 6, 114 and 428 (1911).

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Once the standard buffer mixtures (without indicator) have been prepared, it will be found convenient to keep them in well stoppered and carefully labeled bottles. Thus new color standards may be quickly prepared by adding the indicator to 10 cc. when needed.

THE SYNTHESIS OF TANNING SUBSTANCES.*

By Georg Grasser.

For a conception of the term "Synthetic Tannins" the term "tannin" must first be clearly defined. Under tannin in the narrow sense we mean those products of the vegetable kingdom which are to be found as the water soluble part in many plant organs, they show certain uniform chemical reactions, possess astringent properties and are able to change animal hide into leather. The last-named property of the tannins, to convert the easily perishable protein of the animal hide into a lasting, durable substance and to bestow on it very definite, technically valuable properties, has become decisive for the practical judging of a tanning material. It has been found that different materials show reactions peculiar to the tannins and also are somewhat astringent, without however possessing the important characteristic of being able to tan animal hide. Such materials are to-day suitably called tannin-like substances (for example, coffee-tannin). The decomposition products of the natural tannins to which gallic acid and the hydroxyphenols belong also show the known reactions of tannins without, however, being able to be classed as tannin in the technical and physiological sense.

With reference to their chemical constitution, the natural, true tannins apparently belong to different groups of organic substances, and to-day, with the scarcely investigated chemism of of these substances it is impossible to undertake a chemical classification. After all, however, the assumption is warranted that the true tannins as well as the related lichen substances are ester-like derivatives of phenolcarboxylic acids.[1]

Experiments to produce tannins synthetically, extend in two entirely different directions; one leads either to the synthetic pro-

* Translated and abridged from *Collegium*, 602, 234, 1920.

[1] E. Fischer, B. 46, 3253.

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duction of the simplest tannin, tannic acid (gall nut tannin) or to the construction of substances from phenolcarboxylic acid which possess tannin-like character. The other, entirely new direction, aims at the production of chemical substances, which certainly have nothing in common with the constitution of the natural tannins, but show true tannin characteristics toward animal hide and besides are capable of being produced in large quantity, and are practically utilizable.

Through the constitution of tannin, unknown to us until recently, it is conceivable that experiments to produce tannin synthetically or similar acting tanning materials, were executed variously on a common basis. The oldest research concerning this goes back to H. Schiff,[2] who first obtained tannin-like substances from phenolcarboxylic acid by means of dehydration. By the action of phosphorous oxychloride on phenolsulfonic acid, a good characteristic substance of tanning properties was produced, which he indicated as ethereal anhydride of phenolcarboxylic acid and whose composition was given as $HO.C_6H_4.SO_2.O.C_6H_4.(HSO_3)$. It was scarcely applied, however, to a uniform substance but to a mixture of higher condensation products.

Later Klepl[3] by simply heating p-hydroxybenzoic acid had obtained a so-called di- and tridepside, still this simple process was not applicable to many other phenolcarboxylic acids since these do not endure the high temperature necessary for conversion.

Of other experiments to produce such tannin like condensation products especially those of Gerhardt[4] and Löwe[5] are to be mentioned, who treated gallic acid with phosphorous oxychloride or arsenic acid and obtained amorphous products showing tannin reactions. E. Fischer and Freudenberg[6] also succeeded in producing a didepside through the same treatment of p-hydroxybenzoic acid and later it was these two almost exclusively who investigated the chemical structure of these depsides and produced high molecular polydepsides. The investigation of the constitution of tannin was carried on at the same time and again it was E. Fischer who found its apparent composition to be an ester

[2] *Liebig Ann. Chem.*, 1875, 171.
[3] *J. pr.*, 28, 208.
[4] A., 87, 159.
[5] J., 1868, 559.
[6] A., 372, 45.

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combination of one molecule of glucose with five molecules of digallic acid.

The last named synthetic tannins, which should appropriately be designated as tanning substances to differentiate from the true tannins and which also show a pronounced tannin characteristic toward hide, but constitutionally have nothing in common with the natural tannins, have not only called forth great practical interest through their industrial utilization but also have been fairly exhaustively investigated.

In reference to true tanning action and pickling, the action of chemical substances on the pelt are in need of an exact discrimination. While true tannin action is characterized by the substance penetrating the pelt and being fixed by it in such a way that washing alone is not able to effect a reversion into pelt; pickling has only resulted in a penetration of the pelt to such a degree that by washing out the pickling substance, the pelt is again obtained almost unchanged. Thus it is possible to discriminate in many ways. There are still a number of cases in which we have exemplified a kind of pseudo-tannage which lies between a true tannage and pickling. A substance which is in position to execute such an effect, is, for example, formaldehyde, which for years has found use for hardening animal hide in histological work, since it is easily absorbed by fresh hide from solution and sets it without swelling. At the same time such hide treated with formaldehyde will quickly and strongly absorb true tannins, whereby the pickling effect is established. On the other hand, however, it is characteristic of formaldehyde that it, either alone or better still in alkaline[7] or acid[8] solution, converts pelt into leather; in such formaldehyde tanned leather, however, no tanning material can be detected. Also the yield value which is important for the technical valuation of leather comes out so low that one can hardly speak of it as a tanning material in the practical sense. Accordingly here formaldehyde must be considered as a pseudo-tannin.

According to Thuau,[9] those salts increase the tanning action of formaldehyde considerably more, which form colloidal polymers

[7] Ger. Pat. 111,408.
[8] Ger. Pat. 112,183.
[9] *Coll.*, 1909, 363, 211.

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with it, because these are absorbed by the hide fibrills. The later fact Fahrion conceives in the sense of Nierenstein[10] as true tannage and advances the following scheme:

$$\begin{matrix} \text{R. NH}_2 \\ \\ \text{R. NH}_2 \\ \text{(Hide)} \end{matrix} + \text{O:} \begin{matrix} \text{C.H} \\ \\ \text{H} \end{matrix} = \begin{matrix} \text{R. NH} \diagdown \\ \\ \text{R. NH} \diagup \\ \text{(Leather)} \end{matrix} \text{CH}_2 + \text{H}_2\text{O}$$

A characteristic combination of true tannage and pickling is presented in the tannage with potash alum and common salt, wherein the common salt and salt nature of the alum first of all asserts itself in its pickling action. Simultaneously the alum is split by hydrolysis into its constituents and a part of these is fixed by the hide with a true tanning action.

The two fold action is still more clearly presented with the synthetically produced organic tanning substances, because these contain, on the one hand, colloidal substances of strong tanning action, on the other hand inorganic and organic salts which act together in the manner mentioned.

Condensation of the Phenols.

If phenol is brought together with concentrated sulphuric acid then sulfonation ensues by replacing of the ortho- and para-hydrogen atom and *o*- and *p*-phenolsulfonic acid is formed ($C_6H_4.OH.HSO_3$), the former especially at average temperature which, however, is converted into the *p*- acid by boiling with water.[11] The *m*-phenolsulfonic acid is only obtained in a round about way from *m*-benzenedisulfonic acid [$C_6H_4.(HSO_3)_2$]. Phenol -2.4-disulfonic acid [$C_6H_3.OH(HSO_3)_2$] is produced from *o*- or *p*-phenolsulfonic acid, while phenol -2.4.6- trisulfonic acid [$C_6H_2.OH(HSO_3)_3$] is formed direct from phenol by the action of concentrated sulphuric acid in the presence of phosphorous pentoxide.

Phenolsulfonic acid shows a very great tendency toward condensation and von Baeyer (1872) first employed aldehyde for attaining this reaction. The reaction ensuing herewith is rather violent and resinous bodies, both crystalline and amorphous are obtained. Beside formaldehyde, paraformaldehyde, trioxymethylene, methylal, hexamethylene-tetramine and other sub-

[10] *Coll.*, 1905, 157, 159.

[11] Kekulé, **B. 2**, 330.

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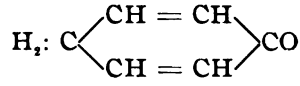
stances which contain a reacting methylene group can be used as well.

A number of these condensation products are derived from diphenylamine or from the phenolic alcohols. If the latter are heated alone or in the presence of acids, then anhydride formation and polymerization take place with the formation of resinous, brittle, fusible substances which are not soluble in water but fairly so in organic solvents. These same materials are formed also in the condensation of phenols with formaldehyde, especially in the presence of acid contact substances and of an excess of phenol, if they are heated long and high enough. For such material the names Novolak, Resole, Resitole and Bakelite have been introduced and they are used[12] as resin substitute, insulating material, and amber substitute either alone or mixed with cork meal, saw dust and the like.

The constitution of these bodies differ considerably according to the nature of the course of the reaction, and the resite of Baekeland, for example, takes the form of a polymerized hydroxybenzlmethyleneglycol anhydride; of Raschig as a diphenylmethane derivative (*e. g.*, dioxydiphenylmethane alcohol); of Wohl as polymerization products of methylene derivatives of the tautomeric phenols.



An entirely separate characteristic property of these bodies is their ability in suitable solution to change animal hide into leather. The author has dissolved in alkali and alcohol a number of such condensation products insoluble in water and could demonstrate good tanning results on pelts with these solutions. Bakelite is dissolved very easily in alkalies and the weakly alkaline solution thus obtained only precipitates gelatine solution a little but after neutralization, completely. Toward iron salts it reacts only with the formation of a dirty brown precipitate.

These condensation products, however, first acquired a particular importance for tanning when Stiasny[13] succeeded in changing them into the water soluble, and thereby into direct tanning

[12] Ger. Pat. 286,568.

[13] Ger. Pat. 262,558.

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form. This is accomplished by subjecting two molecules of concentrated phenolsulfonic acid to the action of one molecule of formaldehyde without letting the temperature exceed 35° C. Since the condensation of these two materials proceeds with liberation of a large quantity of heat, the reaction temperature can only be held within that limit by adding dilute formaldehyde gradually to the phenolsulfonic acid while stirring and cooling.

For the practical production of this tanning material (Neradol D) pure phenol, however, is not used, but its homologue cresol, which, as a technical product, is a mixture of various quantities of the o- m- and p- compound.[14]

In the production of Röchling generator tar from coal considerable quantities of phenols are obtained which can be utilized according to the author for the production of synthetic tannins according to the method of Ger. Pat. 262,558. It produces a deep brown viscous mass which upon neutralization to the usual acidity yields a tanning material similar to Neradol D.

From the course of the chemical process involved in the reaction of phenol or cresol sulfonic acid with aldehyde, it can be concluded that all other homologues of phenol, their polyhydric derivatives, substitution products and acids can also form condensation products in a similar manner. The particular position which aromatic hydroxy compounds occupy in the chemistry of tanning substances, arises not only from the natural system of the tannins, tannin derivatives and their cleavage products, which have been isolated and have been known up to the present time, but also from the other chemical properties of many of these substances. Thus L. Meunier and A. Seyewitz[15] could show that phenol, *p*-amidophenol, chlorophenol, trinitrophenol, pyrocatechine, resorcine, hydroquinone, mono-chlorhydroquinone, orcine, pyrogallol and gallotannic acid give water insoluble precipitates with gelatine and are also capable of tanning in a certain sense. The author has somewhat elaborated this series and has ascertained the conduct of some bodies belonging here as follows:

[14] Ger. Pat. 291,457.

[15] *Coll.*, 1908, 313, 195.

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Substance	Gelatine	Behaviour toward Hide powder	Pelt	
Tribromphenol*	Faint precipitate	Tanning	Superficial	tanning
O-nitrophenol	No "	"	"	"
Brom-nitrophenol	Faint "	"	"	"
Tribrompyrogallol	—— "	"	"	"
Bromophloroglucine	—— "	"	Not	"
Galloflavine	Faint "	"	"	"
Bromo-salicylic acid	" "	"	"	"
Brom-B-Napthol*	" "	"	——	"
Rosolic acid*	" "	"	——	"
Gallic acid	No "	Not "	Not	"

*In alcoholic solution.

In what measure, however, the tanning property of the materials increase, when they, in the form of sulphonic acids, are condensed, can be experimentally shown with nearly every member of this series. Concerning this, however, up to the present the investigations have not been carried out systematically and therefore the author set himself the task to cover this field more thoroughly. The extremely large number of investigations necessary for this and the great difficulty of procuring many of these substances subsequent to the war made a thorough investigation impossible at the present time. In this work the author has collected the little which he was able to work out for general orientation on this domain of research and thus indicate a line for the whole field of research in this direction. Therefore in the following, the transition of some of the most important representatives of this group of substances into methylene condensation products will be discussed with a brief description of their qualitative reactions and tanning property.

The didepside of phenolsulfonic acid can be obtained when carbomethoxyphenolsulfochloride is condensed with sodium phenolsulfonate in the presence of the correct amount of caustic soda. First there is formed a product of the composition

$$CH_3O.C:O.O.C_6H_4.SO_2.O.C_6H_4.SO_3Na$$

that yields by saponification with soda the pure didepside

$$HO.C_6H_4.SO_2.O.C_6H_4.SO_3Na.$$

This can be obtained from its concentrated solution as a white crystalline substance by acidulating. Its solution precipitates gelatine, but is not capable of tanning animal hide.

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However, if the above ester is converted by PCl_5 into the chloride $CH_3.O.C:O.O.C_6H_4SO_2.O.C_6H_4.SO_2Cl$ and this condensed with another molecule of basic sodium phenolsulfonate, then saponified and the solution acidulated and salted out, then the pure tridepside $HO.C_6H_4.SO_2.O.C_6H_4.SO_2.O.C_6H_4.SO_3Na$ precipitates as a white mass, crystallizing in matted needles, which not only precipitates gelatine solution, but is also able to tan pelt.

From the class of durenes, thymol ($C_6H_3.CH_3.C_3H_7.OH$) was converted with concentrated sulphuric acid at 50° C. into the water soluble sulfonic acid and very easily condensed with formaldehyde by moderate warming. The condensation product thus obtained represents a viscous brown mass which is soluble to a clear solution in water and gives the following reactions:

Gelatine—precipitated completely.

$FeCl_3$—blue-black coloration.

Aniline hydrochloride—grayish brown turbidity.

The tanning test with this substance was carried out by first neutralizing it with caustic soda to an approximate acidity of 1 g. = 10 cc. N/10 NaOH, producing a solution of about 2° Bé. from this and then hanging a piece of bated pelt in it. The tanning proceeded in such a way that after 18 hours the pelt was almost tanned, and after 24 hours further it was as fully tanned as the solution would permit. The lightly oiled and dried piece of leather was soft, full and tough and possessed a light grayish brown color.

o-Dihydroxybenzene (pyrocatechol) yields with sulphuric acid a sulfonic acid, well soluble in water, which assumes a deep blue color upon the cautious addition of formaldehyde. This liquid endures heating to 100° C. without precipitating insolubles. However, if some formaldehyde is again added there follows immediately a brownish black color with the precipitation of considerable quantities of insoluble condensation products. On the other hand if the sulfonic acid is diluted a third with water, formaldehyde then added and heated on the water bath, a brown color results with complete union of the formaldehyde to the water soluble condensation product. Its aqueous solution shows the following action:

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Gelatine—precipitated completely.
$FeCl_3$—black-brown coloration.
Aniline hydrochloride—turbidity.

The tanning test with this condensation product which was partly neutralized as in the above test, yielded after a 24-hour period an intense dark coloring of the grain while the inner part of the pelt was white but completely pickled. After 48 hours more this dark color, however, penetrated the whole thickness of the pelt and tanning was completed. The washed and oiled leather was soft, full, tough and possessed an even gray color.

With reference to the dark coloration of a piece of pelt on its conversion into leather by synthetic tanning material, the following condition especially must be referred to. Upon the sulfonation of substances and especially upon their condensation, the formation of a nearly black coloring matter, or of finely divided carbon which is held in colloidal solution, often occurs. If such a substance is dissolved in water and only filtered through a clay filter this material is not eliminated. If this liquid is brought together with pelt, then the latter forms a perfect filter at first and does not let the colloidal material penetrate. Only after tannage of the surface of the pelt with the tanning material of this solution has taken place does the hide filter appear to become more relaxed and allow the colloidal particles to gradually penetrate in, where they are removed by adsorption. In many cases it appears that only traces of such dark colored colloidal particles are present, which are then retained entirely by the surface of the pelt. Following this, only the purified synthetic tanning material penetrates to the interior of the pelt and gives it a white to yellowish brown color.

Meta-dihydroxybenzol (resorcin) can also be easily converted by concentrated sulphuric acid into water soluble sulfonic acids of brown color. If this sulfonation product is then diluted a quarter with water, cooled down completely, treated with a few drops of formaldehyde and heated on the water bath for combination of the formaldehyde, cooled down again, treated with a very little formaldehyde and then heated gradually on the water bath while stirring, then the condensation product is obtained as a mass well soluble in water to a brown color. Its aqueous solution shows the following action:

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Gelatine—completely precipitated.
$FeCl_3$—deep blue coloration.
Aniline hydrochloride—strong turbidity.

The usual tanning test proceeded extremely rapidly and the pelt was completely tanned through in 24 hours with a light brown color. The lightly oiled and dried leather showed a greenish yellow color, was plump, tough and soft.

Para-dihydroxybenzol (hydroquinone) was converted into the water soluble sulfonic acid with concentrated sulphuric acid at 100° C., this treated with a little formaldehyde at ordinary temperature, solidified immediately to a white, solid mass, which was well soluble in water and which had completely fixed the formaldehyde. If this mass, however, was heated for a longer time at 100° C., then a light brown color appeared and the condensation product was less soluble in water. A small excess of formaldehyde and moderate warming leads to dark, violet colored, insoluble condensation products. The aqueous solution of the condensation product shows the following reaction:

Gelatine—precipitated.
$FeCl_3$—deep blue coloration.
Aniline hydrochloride—slight turbidity.

Tanning, carried out in the usual way, proceeded somewhat slower and after a seven-day period only yielded a brown colored, tough and soft leather which still was fairly thin.

Of the trihydroxy-benzenes only pyrogallol and phloroglucine were used in this investigation. Pyrogallol upon sulfonation with concentrated sulphuric acid yielded a violet colored, water soluble sulfonic acid, which when treated with formaldehyde at first while cooling and finally while warming solidified and yielded a deep red-brown colored water soluble mass. The aqueous solution of this product acts toward reagents in the following manner:

Gelatine—completely precipitated.
$FeCl_3$—brownish black coloration.
Aniline hydrochloride—slight turbidity.
Bromine water—no turbidity.
KNO_2—traces of cherry red streaks.

Tanning carried out in the usual manner, yielded after 24 hours a dark colored grain and white, pickled interior, still the dark colored part penetrated the whole pelt quickly and was complete

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in seven days. The resulting leather possessed throughout a dark color, was plump, soft and tough.

Phloroglucine can be converted into the sulfonic acid only very gradually with concentrated sulphuric acid at higher temperatures. This forms a solid mass which is only slightly soluble in water to a wine red color. The gradual condensation with formaldehyde follows in the same way as was described for resorcine, requiring, however, higher temperatures. The condensation product is a brick red powder which is insoluble in water. The same end product is attained if the sulfonic acid is strongly heated alone; herewith condensation ensues with the formation of a reddish brown mass insoluble in water. In high test alcohol, on the other hand, this condensation product is somewhat soluble and forms a reddish brown liquid. Pelt placed in such an alcoholic solution, after 48 hours, was colored on the grain while the interior was only pickled. The continuation of the tanning experiment for four more days produced no change in the appearance of the pelt. Therefore it was taken from the solution, washed lightly with water, oiled and dried when it yielded a gray colored, soft, tough but thin leather. Accordingly there appears to be presented a pseudo-tannage by the very small quantity of synthetic tannin without generally effecting a true tannage and feeding of the pelt.

Independent of these investigations the Elberfelder Farbenfabrik in the meantime have protected a process[16] for the production of condensation products from di- and polyhydroxybenzenes, which may be used for the production of synthetic tannins, but on account of the high cost of condensing the polyhydroxybenzenes, they are only utilizable for pharmaceutical purposes.

In connection with the phenols, quinone may be briefly discussed whose use as a practical tanning material was first described in Ger. Pat. 206,957 of April 30, 1907. According to this process only 400 g. of quinone are used to 100 kg. of pelt and the pelt is tanned with it in five hours in a drum. Leather produced in this matter, in the course of tanning assumes first a red, then a violet, and finally a brown color and its resistance to water, acids and alkalies will be much greater than with all other known tannages. The chemism of this tannage has also given a motive

[16] Ger. Pat. 282,313.

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to theoretical consideration and according to Thuau,[17] in tanning with quinone-like bodies, leather is formed by the quinone entering into reaction with the amido group of the protein molecule with formation of hydroquinone according to the equation:

$$2\,\underset{\text{(Hide)}}{R.NH_2} + 2\,C_6H_4{<}\overset{O}{\underset{O}{}} = C_6H_4{<}\overset{OH}{\underset{OH}{}} + \underset{\text{(Leather)}}{C_6H_4(O.NH.R)_2}$$

Fahrion demonstrated that during quinone tannage the content of active oxygen in the quinone becomes smaller and only the amido group of the hide protein can effect this. Dianilino-quinone might be named as a known analogy.

Distinct quantities of hydroquinone can be actually detected in a used solution of quinone. Hide can also be tanned by saturating with hydroquinone and oxidizing with air. When such hide is taken from the hydroquinone bath and brought into the air, in the presence of alkali, it is colored, first red, then violet, blue and finally brown, and is converted into a quinone tanned leather. There is still to be mentioned that quinone is also able to effect a pseudo-tannage. If quinone is left standing for a length of time with water then a nearly black, amorphous body is formed which is almost insoluble in water, but which is abundantly absorbed by hide powder. However, it is not changed into such an insoluble form as is the case with other tanning materials.

Of the ethereal compounds of the polyhydric phenols, quaiacol, (pyrocatechol-methylether, $HO.C_6H_4.O.CH_3$) was taken in this series of experiments. The conversion into sulfonic acid was carried out by moderate heating with concentrated sulphuric acid and the sulfonation product represented a greenish gray mass well soluble in water. Its condensation by means of formaldehyde was accomplished with the same precautions as has already been described for resorcine; the last traces of formaldehyde could only be brought to combine by a short heating over a direct flame at about 105° C. after the heating on the water bath. Condensation was manifested by the quick appearance of a brownish black coloration of the liquid. The formation of insoluble products could not be perceived. The condensation product is very well soluble in water to a deep brown solution and shows the following properties:

[17] *Coll.*, 1909, 363, 211.

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Gelatine—completely precipitated.
$FeCl_3$—deep brown coloration.
Aniline hydrochloride—slight precipitation.

Tanning proceeded rapidly, so that after 24 hours the pelt was almost completely tanned through with the exception of a narrow white streak. After 24 hours more this streak had also disappeared. The finished leather possessed a dark gray color, was plump, soft and tough. It was similar to that which had been obtained by tanning with the condensation product of pyrocatechol.

From the series of nitro compounds, trinitrophenol (picric acid), $C_6H_2(NO_2)_3.OH$, was investigated. If picric acid in concentrated solution is used for a tanning experiment, the pelt is entirely penetrated by it in a few days. However, oiling of hide tanned in such a manner is difficult since the fat is poorly absorbed. After drying a fairly soft, but thin leather is obtained that easily looses color and tastes intensely bitter. These disadvantages prevent the general utilization of picric acid as a tanning material.

If picric acid is sulfonated with concentrated sulphuric acid and formaldehyde gradually added, then condensation takes place to a water soluble product that precipitates gelatine strongly. By the introduction of bromine, however, a water insoluble product is formed.

The amido compounds as basic nitrogen derivatives of the phenols do not in general belong to those substances which through condensation form water soluble compounds with tanning properties; but on account of their importance some of them were included in this investigation.

Amido-phenol (aniline), $C_6H_5.NH_2$, with concentrated sulphuric acid yields the water soluble sulphate which upon cautious treatment with formaldehyde produces a red colored, water insoluble jelly together with a little of a reddish yellow colored liquid. The latter precipitates gelatine, but does not tan hide. The water insoluble jelly is also insoluble in alcohol and therefore can not be used for a tanning experiment in alcoholic solution.

If dimethyl-aniline, $C_6H_5N(CH_3)_2$, is treated with concentrated sulfuric acid, then a water soluble product results which is not

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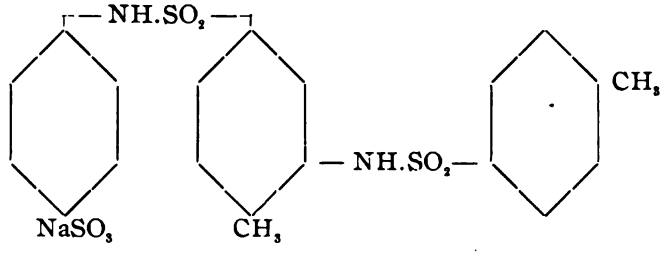
changed by formaldehyde and does not combine with it. It does not precipitate gelatine.

On the other hand if nitrosodimethylaniline, $C_6H_4<^{NO}_{N(CH_3)_2}$, is converted into the water soluble sulfonation product with sulphuric acid and this is boiled a length of time with formaldehyde, then the mass remains soluble in water and precipitates gelatine. A tanning action on pelt, however, could not be established.

Arysulfaminoarylsulfonic acids and arylsulfoxy-arysulfonic acids precipitate gelatine alone but possess no tanning power toward pelt. It only attains this latter property when it contains two sulfamino groups or a multiple or when it possesses besides a sulfamino group, the sulfoxy and still a sulfo group, for example:[18]



Of the aromatic alcohols the di-alcohols show a characteristic behavior because they condense with sulfonic acids with the elimination of water without the assistance of aldehydes. Besides mono-, disulfonic acids and the higher sulfonated products of phenols, the homologous cresols, xylenes and naphthenes[19] also enter into the reaction. The condensation between both components takes place extraordinarily easy with liberation of so much heat that the process proceeds quantitatively. On the other hand dilute solutions are heated to 100° C. and then the process is completed in a few minutes. The products obtained are extraordinarily pure, crystalline and with their precipitability of gelatine show a powerful capability to tan hide. The reaction is as follows:

[18] Ger. Pat. 285,772.
[19] Ger. Pat. 300,567.

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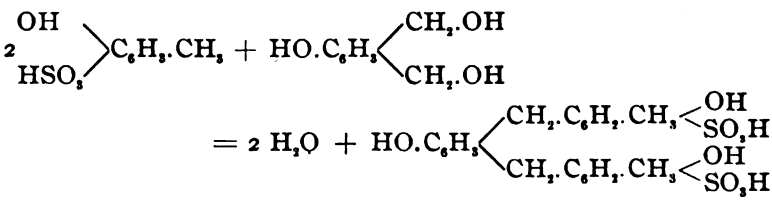

Of the aromatic acids, the behavior of salicylic acid, $C_6H_4.OH.COOH$, is especially to be emphasized. This can be sulfonated very easily at a high temperature by concentrated sulfuric acid and the sulfonated product, which forms a white solid mass, is soluble in water to a completely clear solution. This mass mixed with about a third of its weight of water and treated at 120° C. with formaldehyde, changes rather rapidly into the condensation product. A reddish brown liquid results which is very miscible with water to a clear brown solution. This solution acts in the following manner:

Gelatine—completely precipitated.

$FeCl_3$—deep violet coloration.

Aniline hydrochloride—heavily precipitated.

A piece of pelt placed in a 3° Bé. solution of this condensation product was converted within three days into white, plump and tough leather. Obtaining synthetic tannins from nuclear homologues of salicylic acid is the subject of a patent declaration.[20] Cresotic acid (hydroxytoluic acid), $OH.C_6H_3.CH_3.COOH$, also gives similar results.

If the phenol ester of salicylic acid, $HO.C_6H_4.CO_2.C_6H_5$, is sulfonated a product is formed that is easily soluble in water but which is recognized as a mixture of sulfonation products of salicylic acid and phenol, since sulfonation effects hydrolysis of of the ester. The condensation of this mixture with formaldehyde does not permit the temperature to exceed 80° C. and the aldehyde must be added gradually, since, otherwise, phenol gives rise to a corresponding quantity of insoluble products (Bakelite).

The condensation product dissolved and neutralized to the usual acidity, possesses a very strong tanning action on hide and converts it into a leather in from one to two days, which is very similar to that obtained with the condensation product of salicylic acid.

[20] Ger. Pat. A. 28,901.

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An experiment to produce a condensation product from sodium metahydroxybenzoate with formaldehyde and bisulfite is worthy of note. In this way there was obtained a dark brown viscous mass, which was completely soluble in water to clear solution, showing the following characteristics:

Gelatine—slight precipitation.

$FeCl_3$—bluish black coloration.

Aniline hydrochloride—precipitation.

This condensation product acts toward pelt in the same manner as the phenolsulfonic acid condensation products and also produces a similar leather.

A condensation product of entirely similar action is also obtained from sodium parahydroxybenzoate and formaldehyde with subsequent treatment with sulphuric acid. The products are technically not capable of being used, since only on acidifying do they show a definite tanning action and the presence of free acid gelatinizes the hide. If, on the other hand, uncondensed methane derivatives of phenol, *e. g.*, hydroxyphenylmethane-sulfonic acid, are partially neutralized and a tanning experiment made with such a solution, no kind of tanning action is effected; acidified, it does not precipitate gelatine and ferric chloride only colors it brownish black.

A condensation product of salicylic acid with formaldehyde without sulfonation is possible if it is heated with formaldehyde in the presence of a little hydrochloric acid. The formation of a product slightly soluble in water occurs that can be designated as methylenedisalicylic acid. In an alkaline solution it is very easily soluble and the liquid has an intensively bitter taste. This sodium salt gives a deep violet coloration with ferric chloride, with gelatine a slight precipitate, with aniline hydrochloride a very slight turbidity. Towards hide, however, it shows no tanning action but in alcoholic solution it exhibits a pickling action. Brominated and iodized salts which form a red or reddish brown, clear solution, show a similar action to this.

Gallic acid, $C_6H_2(OH)_3COOH$, heated with sulphuric acid is easily converted into insoluble rufigallic acid, which also in alcohol is only very slightly soluble. But if gallic acid is heated with an excess of sulphuric acid and this mass cooled down and treated with formaldehyde, then a deep brown condensation product is

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formed which is soluble in alcohol and which converts hide into a leather-like, soft but tough product. This condensation product is also soluble in alkali and its solution is likewise capable of converting hide into a leather-like product. Therefore, gallic acid is but little suited to form water soluble synthetic tannins.

Phthalic acid also can hardly be sulfonated. The product treated with sulphuric acid only forms water insoluble condensation products with formaldehyde.

Condensation of Naphthalene Derivatives.

As the phenolsulfonic acids can undergo condensation so also is it possible to condense naphthalene- and naphtholsulfonic acids, with elimination of water, to tanning substances. If naphthalene is heated with sulphuric acid, there is formed, at a lower temperature (about 80° C.) α-naphthalenesulfonic, at a higher temperature (160° C.) and with excess of sulphuric acid, β-naphthalenesulfonic acid which is also formed by heating the α-acid with sulphuric acid. Both of these acids represent deliquescent, crystalline substances. On longer heating of concentrated sulphuric acid with naphthalene the 2.6- and 2.7-naphthalenedisulfonic acids are formed, while a series of isomeric naphthalenetrisulfonic acids are obtained by indirect means. From β-naphthalene sulfonic acid, β-naphthol can be produced; α- and β-naphthols in turn are able to form a large number of α- and β-naphtholsulfonic acids, and mono-, di-, and tri-sulfonic acids. Almost all of these acids represent important raw material for the production of dyestuffs.

The simplest condensation of β-naphthalene sulfonic acid is attained by several hours heating at 135° C. and 20 mm. pressure.[21] The product, obtained thus, is a cheesy mass which reacts very strongly acid. By neutralization of this acid to a lower acidity a gray colored cheesy mass is produced, which is easily soluble in water to a light grayish brown liquid and which reacts in the following manner:

Gelatine—precipitated.
Aniline hydrochloride—precipitated.
Bromine water—no precipitation.

This product shows a good tanning action on hide.

[21] Aust. Pat. 61,061.

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The condensation of β-naphthalene sulfonic acid proceeds much more energetically with the use of formaldehyde. For practical production, the naphthalene sulfonated at 150°-160° C. is condensed with formaldehyde at 85° C., and this condensation product forms the Neradol N of the trade; greater dilution and neutralization brings it to the same tannin content (33 per cent.) as Neradol D and this product appears in trade under the name of Neradol ND.[22] Both products are capable of changing hide in a very short time into a normal leather of white color.

Besides formaldehyde still other substances are able to effect a condensation of naphthalenesulfonic acids. If, for example, sulphur chloride is allowed to act on β-naphthalene sulfonic acid, a light brown solid mass of strongly acid character is obtained. This neutralized as usual produces a grayish brown solid mass, which is very easily soluble in water to a light brown liquid and gives the following reactions:

Gelatine—precipitation.

Aniline hydrochloride—precipitation.

A tanning experiment made with this solution yielded a light brown, fairly soft leather.

Experiments to condense chloronaphthalenesulfonic acid and nitronaphthalenesulfonic acid with formaldehyde, yielded water soluble condensation products, which precipitated gelatine and aniline hydrochloride but only very lightly tanned the surface of pelt.

α-naphthol dissolved in hot concentrated sulphuric acid and heated for some time on the water bath forms α-naphtholsulfonic acid. This moderately diluted with water and mixed cold with formaldehyde, shows no change. On warming the mixture on the water bath a brown precipitation occurs. This turbid liquid treated with gelatine produces a heavy flocculent precipitate. If the turbid solution that has been heated on the water bath is treated with caustic soda, then solution is effected with the formation of a light yellow liquid, which also remains clear after the addition of an excess of acetic acid and gives a heavy precipitate with gelatine. The hot concentrated α-naphtholsulfonic acid treated with sufficient formaldehyde, effervesces violently and yields a dark brown insoluble condensation product which is sol-

[22] Ger. Pat. 290,965.

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uble in caustic soda. This alkaline solution treated with an excess of acetic acid, also precipitates gelatine copiously.

If β-naphthol is dissolved in hot concentrated sulphuric acid and heated sometime on the water bath, then a brown, viscous solution of β-naphtholsulfonic acid is formed. This moderately diluted and mixed with formaldehyde, remains clear but is colored to a dark reddish yellow on heating on the water bath; however, it remains well soluble in water and is abundantly precipitated by gelatine. This condensation product, supersaturated with caustic soda, yields a deep blue solution, which does not precipitate gelatine; on the addition of acetic acid it is colored brown and remains clear and will then precipitate gelatine copiously. If concentrated β-naphtholsulfonic acid is heated on the water bath with formaldehyde then a condensation to a dark reddish yellow, water-soluble mass occurs which will give a copious precipitate with gelatine.

The action of these condensation products in moderately conconcentrated solution on pelt yielded in a few days a light brown leather that is very similar in its properties to vegetable tanned leather.

The practical utilization of the production of synthetic tannins from naphthols and aminonaphthalenesulfonic acids is protected in Ger. Pats. 293,042, 293,640, 293,693, and 303,640.

It is worthy of note that uncondensed methane derivates of naphthols, *e. g.*, β-naphthol-α-methanesulfonic acid, dissolved in water and partially neutralized do not show a tanning action on hide. Also this salt does not precipitate gelatine but with ferric chloride is colored a deep blue. This naphtholsulfonic acid treated with formaldehyde gives a condensation product that is a soluble powder which gives a light yellow slightly turbid solution. This solution only shows tanning properties when it is still weakly acid with sulphuric acid. It precipitates gelatine and aniline hydrochloride. Alkalies give a clear yellow solution without tanning power. Leather tanned with the acidulated solution very much resembles neradol D tanned leather but the color is somewhat streaky.

If β-naphthol is condensed with hydrochloric acid and formaldehyde, then an insoluble methylenedinaphthol is formed whose sodium salt is well soluble in water. The same condensation,

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however, is also obtained in alkaline solution when the sodium salt is formed direct. The condensation product precipitates gelatine and ferric chloride with bluish gray color; acids again precipitate the insoluble methylene product. It tans hide very rapidly with separation of insoluble products and a soft white plump leather is obtained which is not very tough.

Condensation Products of the Anthracene and Phenanthrene Groups.

Anthracene heated with an excess of sulphuric acid produces the well soluble anthracene-disulfonic acid. If this is condensed hot with formaldehyde then water soluble, reddish brown colored condensation products are formed, which on longer heating with formaldehyde are converted into insoluble substances. The aqueous solution of the condensation product does not show a precipitating action and only gives with gelatine solution a flocculent precipitate, and with copper sulphate a green precipitate which is soluble in excess to a blue color. The partially neutralized solution is capable of tanning the exterior of hide in eight days and effects a kind of pseudo-tannage in the interior. After drying of the hide treated in this manner, a leather is obtained that is brown colored on the outside, is plump and soft but not very tough. It is concluded from this that this condensation product represents more of a pickling than a true tanning material.

Anthraquinone, $C_6H_4.CO.CO.C_6H_4$, treated with concentrated sulphuric acid and with formaldehyde in the hot yields a mass that is only soluble in water to a milky solution. This will not become clearer through the addition of an excess of caustic soda. The aqueous solution gives the following reactions:

Gelatine—complete precipitation.
Aniline hydrochloride—complete precipitation.
$Ca(OH)_2$—dark gray precipitate.

All other tannin reagents give no reaction. The moderately neutralized solution of the condensation product shows principally a pickling action on hide, while it tans the surface with a light brown color, the rest of the hide is white and pickled. During the tanning experiment the separation of insoluble products occur which leads to the almost complete separation of all

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originally dissolved material. The treated hide yields a light brown, moderately soft, plump leather that is not very tough, which can be washed only with difficulty and that has more the character of pickled hide.

1-hydroxyanthraquinone, 1.5-dichloranthraquinone, 1.5-diamidoanthraquinone, 1-methylaminoanthraquinone, 1-benzoylamino-6-chloranthraquinone, 1-meta-toluido--anthraquinone and 1-anilidoanthraquinone yield throughout, on condensation with sulphuric acid and formaldehyde, products that are but little soluble in water and which do not precipitate gelatine. Individual tests to dissolve these condensation products in alcohol and to carry out tanning experiments with them only yielded poor leather of a decided pickled character. 1-methylamino-4-bromanthraquinone condensed with sulphuric acid and formaldehyde likewise gives rise to a condensation product that is little soluble in water, but which precipitates gelatine copiously.

Phenanthrenequinone heated with much concentrated sulphuric acid for a long time gives rise to a water soluble, reddish yellow product. This treated in the cold with formaldehyde and finally heated, strongly fixes the formaldehyde very gradually and forms a water soluble mass. If, however, the heat is maintained longer, then water insoluble products are formed which are neither soluble in caustic nor in alcohol. The aqueous solution of this condensation product gives no reaction with the usual tannin reagents but precipitates gelatine completely. The partially neutralized solution pickles pelt very rapidly producing a light brown color and pelt taken from the tanning bath after several days forms after drying, a brown fairly plump, soft and tough leather. If this condensation product in hot aqueous solution is subjected to the action of bromine, it will be added well and the reaction product remains soluble in water. The aqueous solution of this brominated product likewise does not give noteworthy reactions with the usual tannin reagents but precipitates gelatine completely. Pelt subjected to its action is penetrated much slower, only the surface is colored brown, the interior is pickled with a light brown color. After the treated pelt is dried there results a hard, empty but tough leather that shows predominantly the character of pickled pelt.

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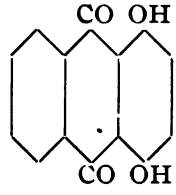
In conclusion, there are to be briefly mentioned here the following experiments:

Quinizarin,  , treated with sulphuric acid and formaldehyde gives a condensation product that is only slightly soluble in water, which does not precipitate gelatine.

Quinoline sulfonated and condensed with formaldehyde gives a reaction product that is completely soluble in water to a clear dark colored solution, which does not precipitate gelatine. It acts similar to hydroxyquinoline. On the other hand the technical production of a synthetic tannin from retene (methylisopropylphenanthrene) is protected in Ger. Pat. 290,965.

Di- and Triphenylmethane Groups.

If diphenylmethane, $(C_6H_5)_2CH_2$, is treated with a quantity of hot sulphuric acid a bluish black mass, well soluble in water is formed. This heated a little with a little formaldehyde yields a brown fluid, which also endures a stronger heating after condensation. If this mass is again treated with formaldehyde then the formation of brown water insoluble masses ensue. The aqueous solution of the condensation product precipitates gelatine completely and aniline hydrochloride. A tanning experiment made with this solution shows a moderate tanning ability. The pelt is colored well throughout and is rapidly pickled. The leather taken from the tanning liquid after four days yields, after drying, a grayish brown, discolored leather that is slightly plump, fairly hard and not very tough.

On the other hand the production of a synthetic tannin from carbazol (dibenzopyrrol) found a practical application which is protected by Ger. Pat. 290,965.

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Triphenylmethane, $(C_6H_5)_3.CH$, treated in the hot with excess of sulphuric acid gives a nearly black mass, which when condensed first at ordinary followed by a higher temperature with formaldehyde, yields a mass that is fairly well soluble in water. Its solution precipitates gelatine completely. A tanning experiment conducted with the partially neutralized solution, showed a tanning action similar to that established for diphenylmethane. The leather obtained after tanning possessed a black color, but was soft, plump and tough.

The observations of Baeyer[23] that pyrogallol forms through condensation with formaldehyde an amorphous compound soluble in water which precipitates gelatine and acts in the same manner as tannin was later confirmed by Caro[24] and Kahl.[25] The latter found that through the condensation with formaldehyde of phenols or phenolcarboxylic acids, diphenylmethane derivatives are formed. Nierenstein[26] has repeated this experiment and besides the insoluble diphenylmethane has also obtained a water soluble, gelatine precipitating compound. The condensation product of gallic acid proved to be hexahydroxyaurincarboxylic acid,

$$\begin{array}{l} \quad\;\; / C_6H(OH)_3.COOH \\ C — C_6H(OH)_3.COOH \\ | \quad\;\; \rangle C_6H(OH)_3.COOH \\ O \end{array}$$

which is formed together with hexahydroxydiphenylmethanedicarboxylic acid, $C_6H(OH)_3COOH.CH_2.C_6H(OH)_3COOH$. By Baeyer's mode of procedure with pyrogallol according to Nierenstein a compound of the following composition is also apparently formed:

$$\begin{array}{l} \quad\;\; / C_6H_2(OH)_3 \\ C — C_6H_2(OH)_3 \\ | \quad\;\; \rangle C_6H_2(OH)_3 \\ O \end{array}$$

and in these compounds Nierenstein found a support for his assumption of tannophors—CO—in the tannins. Stiasny[27] and Kauschke[28] supported this assumption and the latter states that these easily soluble compounds tan. Nierenstein[29] then further established that

[23] B., 1872, 5, 280 and 1096.
[24] B., 25, 947.
[25] B., 31, 114.
[26] *Coll.*, 1915, 221.
[27] *Gerber*, 1905, 233.
[28] *Coll.*, 1906, 362.
[29] *Coll.*, 1906, 434.

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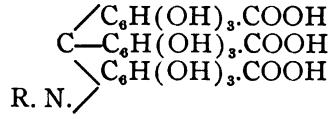
all condensation processes between formaldehyde and phenols or hydroxycarboxylic acids form besides the water insoluble hydroxydiphenylmethanes or hydroxydiphenylmethanecarboxylic acids, compounds of the character of the hydroxyaurines or hydroxyaurincarboxylic acids which possess a decided tannophor and therefore give a precipitate with gelatine, that is, effect tanning. Also if leather formation is represented as Schiff's base[30] then the hexahydroxyaurincarboxylic acid leather can be formulated in the following manner:



Through the production of this and similar condensation products Nierenstein and Webster[31] could observe a characteristic action of the carboxyl group. 2.5 g. of every phenol or acid concerned was dissolved in 300 cc. of water and while boiling 5 cc. of formaldehyde (20 per cent.) and 2.5 cc. of hydrochloric acid added in drops; the precipitate formed was filtered off after 24 hours, dried to constant weight at 110°, extracted well with hot water, filtered hot and the residue again dried at 110° and weighed. Thereby the following values were found:

	Total precipitate grams	Water-insoluble diphenylmethane derivatives Per cent.	Water-soluble hydroxyaurine-carboxylic acids Per cent.
Phloroglucine	2.4002	100	——
Hydroquinone	2.3716	100	——
Pyrogallol	2.5150	100	——
Pyrocatechine	2.9805	100	——
Resorcine	2.9954	100	——
Gallic acid	2.0706	78.84	21.16
β-Resorcyclic acid	2.1040	51.08	48.92
Protocatechuic acid	0	——	——
Vanillic acid	0	——	——
Tannin	2.0599	——	100
Digallic acid	2.1042	80.16	19.84
Leuco-digallic acid	2.0041	1.94	98.06

The ability to condense to diphenylmethane derivatives decreases with the appearance of carboxyl group and is even zero for

[30] *Coll.*, 1906, 159.
[31] B., 1908, 41, 80.

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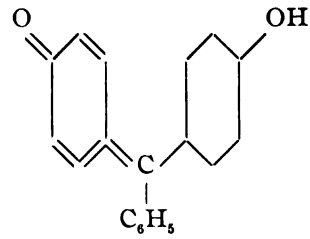
protocatechuic acid. Nierenstein sees in this reaction an analogy to cork formation, to whose genetic connection with diphenylmethane formation Drabble and Nierenstein[32] have referred earlier It is possible that the plants to free themselves of the poisonous water soluble phenols and aromatic hydroxycarboxylic acids (also tannins) besides using the oxidation processes (formation of phlobaphenes, ellagic acid, etc.), also make use of formaldehyde as methylating reagent for the formation of these insoluble condensation products.

The behavior of phenols to aldehydes was also examined by the following investigators: Michael[33] produced a condensation product from phenol and resorcine with benzaldehyde, and Russanow[34] likewise from phenol and benzaldehyde. Lipp[35] investigated the behavior of benzaldehyde and piperonal on phenol, anisol, cresols, cresol ether, resorcine and their esters and determined that by condensation with benzaldehyde of the free phenols, the hydroxyl groups remained in the same positions as by the action of the corresponding phenol ethers on the aldehyde. Dihydroxytriphenylmethane derivatives thus obtained form beautiful crystals which are changed by oxidation agents into benzaurines. The constitution of these oxydation products apparently corresponds to the following formula:



In alkalies the hydrolyzed triphenylmethanes are colorless, with concentrated sulphuric acid, on the other hand they assume more intensive coloring.

If the hydroxyl groups are found in the ortho position to the methane residue then they can form by elimination of water, xanthenes of the following constitution:

[32] *Biochem. J.*, 1907, **2**, 96.
[33] *Amer. Jour.*, **5**, 338, and **9**, 130.
[34] B., **22**, 1944.
[35] *Diss. Bern*, 1905.

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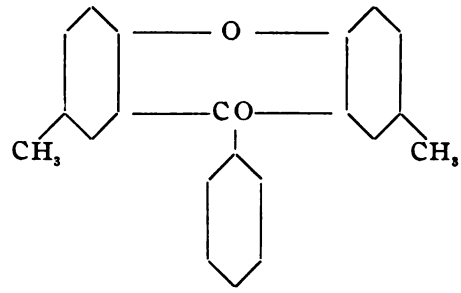
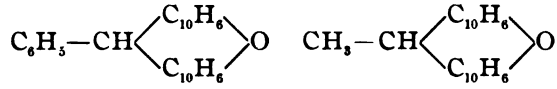


In the benzene series this reaction is executed with considerable difficulty and only takes place on the distillation of the dihydroxytriphenylmethane concerned at ordinary pressure.

In the naphthalene series, on the contrary, closing of the ring takes place on the condensation of β-naphthol with benzaldehyde or paraldehyde and leads to the following substances:



These xanthenes are white, silky, lustrous needles, which are insoluble in water and alkalies. By concentrated sulphuric acid, on the contrary, they are dissolved with a beautiful fluorescence.

Summary.

From the description of the individual properties of the different condensation products it is seen that to stipulate gelatine precipitation and absorption of the substance by hide powder does not hypothecate a tanning action on hide. Thus for example, hydroxynaphthylmethanesulfonic acid precipitates gelatine, but has no tanning action on pelt. Sodium dicresylmethanedisulfonate, on the other hand does not give a precipitate with gelatine and also does not tan hide but is absorbed by hide powder as "tanning substance." A substance, which does not precipitate gelatine but nevertheless has some tanning action on hide powder and pelt was found in *o*-nitrophenol.

With reference to the capability of forming condensation products with tanning properties the following can be briefly stated:

All mono- and polyhydric phenols can be converted into true tanning agents by condensation with dehydrating substances before or after converting into soluble sulfonic acids. The end

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effect remains the same whether the condensation takes place first and then converting this insoluble product into a water soluble product by sulfonation or, vice versa, by condensing the sulfonic acids. The alkaline solution of phenols also can be condensed by means of dehydrating agents and will yield after acidulation of the reaction product, a water soluble tanning material; the same is successful with the use of aldehydes.

Of the substitution products of phenols the thio-, chloro-, bromo-, nitro-, and amido- derivates in general give effects similar to tanning materials.

Quinone as it is represents a tanning substance.

The aromatic di-alcohols condense very easily with the different sulfonic acids and yield very valuable tanning agents.

Of the aromatic acids, all those appear to give a technically utilizable tanning agent by condensation which yield water soluble products on sulfonation; where that is not the case, their water soluble alkali salts can be condensed with formaldehyde and these substances then represent tanning agents when they endure neutralization to a neutral or weakly acid liquid without being precipitated.

The diphenyl derivates show tanning properties when they belong to the previously mentioned groups.

The same is true for the compounds with condensed neuclei and all their derivatives, which correspond to the above requirements.

The kind of condensation agent is, in general, of no special influence. The elimination of water by ordinary heating is only partially successful since the temperature necessary for this reaction causes a decomposition of the substance in many cases. This evil can be avoided in many cases by the use of reduced pressure.

Condensation with formaldehyde succeeds in all cases, with acetaldehyde and benzaldehyde only occasionally. The remaining dehydrating agents (sulphur chloride, phosphorous compounds, etc.) likewise, in general, lead fairly easily to condensation, but the color of the tanning agent and of the leather produced by them is unfavorably affected in many ways by the formation of secondary products G. W. S.

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ABSTRACTS.

The Swelling of Gelatine in Acids. By W. R. ATKIN, *J. S. T. C.*, 4, 248 (1920). The writer compared the results obtained by direct swelling experiments on gelatine left for 48 hours in solutions of various acids (all monobasic) of varying concentrations but carried out by different workers at different times. By curves it is shown that maximum swelling occurs at a definite hydrion concentration even for such widely differing acids as formic and hydrochloric acids. The curves indicate that acetic acid might also show a maximum swelling if solution of the gelatine did not occur in the strong solution that is necessary to obtain a hydrion concentration of $[H\cdot] = 0.004$ normal, or $P_H = 2.4$.

The quantity *e* described by Procter and Wilson which represents the excess of the concentration of diffusible ions in the jelly over that of the external solution, and which has been shown to be proportional to the swelling power, also exhibits a maximum value corresponding to a P_H value of 2.4 for a calculated theoretical external acid solution. The point of minimum swelling has been shown by several observers to be at $P_H = 4.6$ which is the isoelectric point of gelatine.

From the above considerations both the quantity *e* and the swelling are shown to be functions of the hydrion concentration of the external acid solution and the similarities pointed out by Procter and Wilson have been confirmed quantitatively.

The Tannin of Knopper Gall. By M. NIERENSTEIN, *J. Chem. Soc.*, 1919, 1174-1180; *Chem. Abstr.*, 1920, 475. The tannin was extracted from the fat free galls with acetone. The extract was diluted with acetone and the tannin preciptated by adding light petroleum. The tannin was further purified by reprecipitation.

Properties of the pure tannin:—Soluble in alcohol, acetone, ethyl acetate, acetic acid and water. Insoluble in benzene, chloroform and light petroleum. A greenish blue color was given with ferric chloride and the tannin is quantitatively adsorbed by caseinogen. Molecular weight determinations in acetone solution were:—1628, 1654, 1708 and in alcoholic solution 1744, 1682, 1664. Hydrolysis with dilute acid gave ellagic acid and dextrose. The methylated tannin was an amorphous colorless substance having no definite melting point. Methoxy group determinations gave 36.9, 37.4, 37.2, 37.8.

Hydrolyzed with 10 per cent. alcoholic potash, the methylated tannin gave products both soluble and insoluble in benzene. It is concluded that the tannin is composed of luteoic acid and dextrose. *J. S. L. T. C.*

The Tannin of Canadian Hemlock (Tsuga Canadensis). By M. NIERENSTEIN and R. J. MANNING, *J. C. S.*, 1919, 662; *Chem. Abstr.*, 1920, 1460. The tannin was extracted with cold acetone, the solution concentrated and diluted with water to preciptate the phlobaphenes and the filtrate concentrated under reduced pressure. Remaining phlobaphenes were precipitated by dissolving the residue in alcohol and again pouring into water. This operation was repeated, and the tannin recrystallized from acetone. This

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was a pink amorphous substance decomposing at 260° C. It was soluble in alcohol, acetone and water and gave a red solution. No sugars were formed on hydrolysis, but protocatechuic acid was found. Alkaline hydrolysis of the methylated tannin gave opianic acid. Alkaline hydrolysis of the brominated tannin with alcoholic KOH (not a single compound) an acid was produced which has provisionally been termed monobromotsuginic acid having the probable constitution $COOH.C_7H_5OBr.OH$.

J. S. L. T. C.

Tannins. V. Phloroglucinol Tannins and Catechins. Constitution of Gambier Catechin. By K. FREUDENBERG, *Ber.*, 1920, **53**, 1416-1427. Gambier catechin has been considered by Kostanecki to be a derivative of ethyldiphenylmethane, mainly on account of its reaction with diazonium salts. By the action of sodium and alcohol on its tetramethyl ether and subsequent methylation, a crystalline pentamethyl ether is produced which Kostanecki regarded as 3-ethyl-2.4.6-trimethoxyphenyl-3'.4'-dimethoxyphenylmethane, but which is now shown to be 2.4.6.3'.4'-pentamethoxy-$\alpha\gamma$-diphenylpropane. Hence, like the nearly related flavone dyes, anthocyanidins and phenyl styryl ketones, gambier catechin must have an $\alpha\gamma$-diphenylpropane skeleton. *J. S. C. I.*

Relation Between Hydrolysis and Adsorption, I. By W. MOELLER, *Coll.*, 109, 152, 209, 267 (1920). The action of acids on hide powder is first one of hydrolysis, which proceeds much more quickly and strongly with inorganic than with organic acids. The presence of neutral salts appears to check the hydrolysis at first and then suddenly facilitates it. Besides the hydrolysis adsorption takes place between the non-hydrolyzed protein micells, the products of hydrolysis, combined and uncombined with acid ions, and ionized and un-ionized protein molecules. The swelling is due to the increase in volume of the micellar strands caused by the adsorption of hydrated protein ions by the unattacked collagen micells in the hide substance. By the addition of neutral salts the hydrated hydrolyzed collagen ions in the solution are dehydrated and no swelling can take place, although there may be subsequent adsorption. The effect of ampholytes on the hide powder is to restrict the hydrolysis. The apparent acidity of hide powder which has been in contact with acid for an hour and is then titrated in presence of different indicators differs from the actual acidity and forms no guide to the true conditions of the processes going on. With gelatine very different results are obtained owing to structural and chemical differences between gelatine and hide powder. *J. S. C. I.*

Relation Between Hydrolysis and Adsorption, II. By W. MOELLER, *Coll.*, 319, 382 (1920). The action of acids and alkalies on proteins, which is so frequently represented as being parallel to the adsorption process in dyeing and tanning, is quite different and cannot be cited as evidence for the chemical theory of tanning. The substances used in dyeing and tanning are either neutral or so feebly acid that hydrolytic effects on the animal fibers are either excluded or very much repressed. *J. S. C. I.*

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Lignin. III. Preparation of a Tannic Acid from Lignosulphonic Acids. By M. HÖNIG and W. FUCHS, *Monatsh. Chem.*, 41, 215-222 (1920). The barium salts of the three fractions of the lignosulphonic acids are converted by boiling aqueous barium hydroxide solution into different insoluble compounds, which have not been identified, and a single soluble salt, $C_{18}H_{30}O_{10}SBa$, the acid corresponding to which has the character of a tannic acid of the catechu group with properties which are somewhat modified by the sulphur content; when fused with potassium hydroxide, it gives protocatechuic acid in good yield. *J. S. C. I.*

Conductometric Titration of Phenols. By I. M. KOLTHOFF, *Z anorg. Chem.*, 112, 187-195 (1920). Phenol and cresols can be accurately titrated in N/10–N/100 solution with alkali by the conductometric method. The hydroxy group in vanillin, sodium phenolsulphonic acid, salol, and methyl salicylate can be similarly titrated. Salicylic acid behaves as a monobasic acid, the hydroxy group having no acidic character, but *p*-hydroxybenzoic acid behaves as a dibasic acid. The hydroxy group in thymol and β-naphthol can also be titrated conductometrically. Catechol behaves as a monobasic acid, the second hydroxy group having no acidic properties, whilst resorcinol and quinol are dibasic. Resorcinol is best titrated with barium hydroxide; when sodium hydroxide is used the breaks in the conductivity curve are not distinct. Pyrogallol and phloroglucinol function as dibasic acids and gallic acid as a tribasic acid. *J. S. C. I.*

Determination of Ammonia in Oil and Fat Preparations. By N. WELWART, *Chem.-Zeit.*, 44, 719 (1920). To determine ammonia in Turkey-red oil and similar products in which free acidity has been neutralized with ammonia, the sample is mixed with water and an excess of calcium chloride solution, a few pieces of pumice-stone and a sufficient quantity of sodium hydroxide are added, and the mixture is distilled, the ammonia being collected in standardized acid. The calcium soaps formed do not froth during the distillation. Light mineral oils, if present, may pass over into the distillate, but do not interfere with the determination. Methods which depend on the extraction of the ammonia by shaking the oil with dilute acid and subsequent distillation of the acid extracts with sodium hydroxide are not always trustworthy, since certain sulphonated oils contain the ammonia in such combination that it is not extracted even by boiling with acidified water. *J. S. C. I.*

Synthesis of Humic Acids. By W. ELLER and K. KOCH, *Ber.*, 53, 1469, (1920). The oxidation of phenols in alkaline solution leads to the formation of substances which have all the properties of natural humic acids. Thus solutions of catechol, quinol, or *p*-benzoquinone when exposed to air or treated with solid potassium persulphate give a product of the composition, $C_6H_4O_3$, whilst phenol gives a similar humic acid which is distinguished, however, by its greater solubility in alcohol. In general, only those phenols give humic acids which are capable of yielding quinonoid

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intermediate products. It would thus appear that there are a number of natural humic acids and that these substances when pure are free from nitrogen, and their acidic properties are probably due to the presence of an unchanged phenolic hydroxy-group. *J. S. C. I.*

A Test for Synthetic Tannins. By R. LAUFFMANN, *Coll.*, 600, 169-171 (1920). The indophenol reaction cannot be used as a specific test for Neradol D or ND, since there are now many synthetic tannins made from raw products similar to those used in making neradol and which would therefore respond to this test. But the test, modified as described below, can be used for that class of synthetic tannins formed by the condensation of formaldehyde with the sulphonic acids of phenol, cresol, naphthalene or anthracene respectively. Extract 10 gms. of the finely divided leather twice with 100 cc. portions of 2 per cent. sodium hydroxide. Neutralize this extract with sulphuric acid, evaporate to dryness and add the pulverized residue to 20 cc. of 1 : 1 potassium hydroxide contained in a large silver crucible. Heat the crucible at first over a low flame, then strongly until only a lumpy brittle mass remains. Treat this mass with sulphuric acid until effervescence ceases, add sodium hydroxide until almost neutral, then add 100 cc. of 10 per cent. ammonia and cool. Extract this liquid twice with half its volume of ether, breaking up emulsions with hot alcohol, distil off the ether and dry the residue for ¼ hour. Dissolve the residue in 6 cc. of hot alcohol and divide the solution between 3 watch glasses in the ratio of 1 : 2 : 3 finally diluting each to 4 cc. To each watch glass add 2 drops each of 0.6-0.7 per cent. aqueous solution of paraphenylenediamine hydrochloride and a 5 per cent. solution of potassium ferricyanide. A positive reaction is shown by a weak or strong blue or sometimes a greenish color. If the solution is cloudy the test is made more delicate by filtering through a small filter. If a liquid or a tanning extract is to be tested, evaporate a portion to dryness and use 2 or 3 gms. of the residue for the fusion with potassium hydroxide. Then proceed as in the test of leather. The fusion with potassium hydroxide not only liberates the phenol from the sulphonic acid but also destroys most of the organic substances which interfere with the test. Also by making the solution ammoniacal before extracting with ether, the extraction of all but very small amounts of substances other than phenols is prevented.
I. D. C.

Aldehyde Tannage, V. By W. MOELLER, *Coll.*, 601, 185-199 (1920). The author states that Gerngross (*Coll.*, 1920, 2) has assumed that hide substance reacts like a simple soluble chemical substance, while previous work (*Coll.*, 1918, 137 and 365) has shown that albumins are not chemical individuals. Also in the preparation of hide powder from hides, especially in bating, there are formed decomposition products from the most complex down to amino acids, and these are absorbed by the unchanged hide substance. The formol titration only estimates the hydrolyzed nitrogenous matter and does not show whether there is either a chemical reaction

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between formaldehyde and the unchanged hide substances or an adsorption of formaldehyde by the latter. The author with the assistance of Dr. Büttner investigated the adsorption of acid by untreated and by formaldehyde treated hide powder, and also determined the nitrogen and from this the hide substance which had gone into solution. The concentration of the acid was varied from tenth normal to normal and the time of contact between the hide powder and acid was varied from two minutes to two days. With tenth normal hydrochloric acid in two minutes, the formaldehyde treated hide powder adsorbed slightly less acid than the untreated, but in all other cases the formaldehyde treated hide powder adsorbed more acid, the difference between the two being greater the stronger the acid and the longer it was allowed to act. The hydrolyzed hide substance also increased with time and concentration of acid and reached 2 per cent. in two days with normal acid and the formaldehyde leather. When the experiment was repeated, using sodium hydroxide in place of hydrochloric acid, more sodium hydroxide was found to be taken up by the treated than by the untreated hide powder. The hydrolysis of the treated powder reached 20 per cent., while that of the untreated leather reached 77 per cent. The influence of time is probably due to the fact that, while "equilibrium" between the methyleneamino acids and hydrochloric acid is reached in a few minutes, the adsorption of acid continues for some time. The amino acids are also adsorbed by the unchanged hide powder and so lower the acidity of the solution, but the extent of this adsorption is not known. The fact that Gerngross obtained varying decreases in the adsorption by hide powder of equimolar quantities of various acids is believed by the author to be due to the different hydrolyzing effect of the various acids. Strong acids have a greater hydrolyzing action than weak acids and the hydrolytic products reacting with formaldehyde form amino acids, which increase the acidity of the solution and therefore decrease the apparent adsorption. That the tanning process with formaldehyde is similar to any other tanning process, was shown by treating hide powder with varying concentrations of formaldehyde for periods of time ranging from fifteen minutes to two days. In dilute solution very little formaldehyde was taken up. This agrees with the known fact that a weak formaldehyde solution has almost no tanning action. The amount of formaldehyde taken up increased with the concentration and with the time up to twenty-four hours. In a similar experiment in which both the formaldehyde and hide powder were neutralized with sodium hydroxide, there was an immediate adsorption of formaldehyde, which reached a maximum in six hours. The author states that the decrease in adsorption after six hours is probably due to the formation of formic acid from the formaldehyde by Cannizzaro's reaction, and this formic acid would be estimated as formaldehyde since the hydrogen peroxide method was used. He is still of the opinion that the aldehyde reacts chemically with the decomposition products, forming soluble compounds which have no tanning action, and that the tanning factor is the insoluble polymers and condensation products formed from the excess formaldehyde. I. D. C.

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A Rapid Method for the Determination of Nitrogen in Leather. By FINI ENNA, *Coll.*, **601**, 207-9 (1920). The determination can be completed in 2 hours by the following method, which has been used for some years by the laboratory of the Royal Agricultural Institute for determining nitrogen in substances other than leather. 8-10 gms. of nitrogen free potassium sulphate and 20 cc. of concentrated sulphuric acid are added to 1 gram of the leather, divided into 6-8 pieces, and the mixture is heated over a low flame. When the leather has separated into fine particles (about 10 minutes) a small drop of mercury is added and the heating continued until the solution is light yellow. The mercury is then precipitated with either potassium sulphide or glucose, and the ammonia is distilled into a saturated boric acid solution and titrated with N/10 hydrochloric acid, using congo red as the indicator. I. D. C.

Defects of Chrome Leather. By B. KOHNSTEIN, *Häute und Lederberichte*, 1919, 51; through *Coll.*, **603**, 346-8 (1920). Some of the defects from unsound hides are discussed together with the causes of defects in chrome tanning. Too short a soaking with insufficient mechanical working to bring the skins in a uniform condition will cause hard horny spots. Hard, thin leather will result from the one bath process if the chrome liquor is not sufficiently basic, and similar spots will occur where the edges of the leather from the pickle or chrome liquor have been allowed to dry out. Storing of the skins during process in high piles will also cause flat leather from the bottom ones. The unhaired skins, especially from the reduction bath, should be piled as smoothly as possible, otherwise wrinkles or folds will form. The skins from the chrome liquor should not be unduly exposed to the light as flat spots will result from a partial tannage of the exposed places. The direct addition to the pickle or reduction bath of too concentrated acids may cause hard brittle spots. Chrome leathers are subject to several kinds of spew which can originate from mineral matters as well as fats. In the two bath process the free sulphur may form a coating on the leather which is rendered more conspicuous by glazing and ironing. Some spews can be readily wiped off, but they almost always reappear in a short time. Oiling off of the finished chrome leather with hot mineral oil will prevent the recurrence of fat spew. To avoid spewing the chrome leather should be carefully freed from soluble salts, carefully neutralized, and only good oils and soaps used for fat-liquoring. For the latter may be mentioned neatsfoot oil, moellon, degras, also esters and higher oxidation products of the vegetable oils and the liquid animal waxes as spermaceti oil. Sulphonated neats and castor oils, egg-yolk oil and water soluble mineral mixtures with soap solutions are also used. Frequently with stuffed black leathers, small drops of fat form on the surface due to the free acid in the leather decomposing the soap solution and liberating the fatty acid, which in part deposits on the surface of the leather. Fat spews may also occur when dyestuffs, containing gums or dextrine which clog the pores of the leather, are used, and also from small lumps of fat in the fat liquor. Spew often becomes more evident

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if the leather is laid away for some time in high piles so that the droplets of fat run together and form irregular patches on the grain which on glazing become even more conspicuous. It is best in such cases, before glazing, to scour the grain with dilute lactic, citric, tartaric acids or barberry juice. Fat spew is very probable if the free fatty acid from wool grease is used, since this congeals at 40° and the unsaponifiable portion of the wool grease readily forms lumps, which deposit on the surface of the leather. The natural fat of the skin, especially with those from sheep and goats, may be another cause of spewing if provision is not made in the liming and bating for the complete saponification of the natural fats and the decomposition of lime soaps. Fungus growth, particularly from the aspergilli, mucors, and pennicilli, give rise to circular spots on the leather known to the tanner as mildew. It appears when the leather is stored in damp rooms; put away in a damp condition; or laid in musty sawdust to soften for staking, and is best overcome by wiping off with dilute phenol or formaldehyde. A loose easily removed grain may occur, especially with old ox or cow hides and should be guarded against by avoiding undue swelling and strong long liming. Strongly basic chrome liquors will also cause loosened grain so that it is best to set the grain with very weakly basic liquors and gradually render them more basic by slow addition of soda. Unequal stuffing and staking of the leather will produce a non-uniform grain and in places a loose grain layer. The repeated application of a thick seasoning to the dry grain before glazing and in addition incorrect temperature in the drying room, will likewise cause loosened grain. R. W. F.

"Rifflige" (Pipey) Grain on Chrome Leather. By W. Eitner, *Häute und Lederberichte*, 1920, 153; through *Coll.*, 603, 351 (1920). The author discusses the so-called pipey grain defect which formerly often occurred with glove leather and later also with chrome leather. The defect occurs as a peculiar wrinkled formation of the grain similar to that which is met with in many sheepskins as "ribby" skins. This ribby formation occurs broadwise across the skin and the wrinkles so formed can be worked out so that in dyeing the color is uniformly taken up. With the "riffligen" (pipey) grain, however, the folds or wrinkles extend lengthwise of the skin and do not yield to a uniform working up of the skin so that in dyeing the ridges and depressions take up the color unevenly and give a streaky grain. With the finished leather even upon glazing the streaks are evident. These defects are due to insufficient working of the skins during soaking, staking, liming and bating so that the inner part of the skin remains too firm and the grain cannot lay down sufficiently smooth. The author describes the measures to take to avoid this fault.

R. W. F.

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PATENTS.

Leather-Working Machine. U. S. Patent 1,354,572. F. M. McCarthy, St. Louis, Mo. Filed Oct. 4, 1919.

Process of Tanning Fur. U. S. Patent 1,355,374. T. O. Williams, Pasadena, Cal. Filed Oct. 17, 1918. The process of tanning furs, which consists in first brushing the skin side of the preliminary cleansed fur with a diluted extract of poke root until the hide is thoroughly moistened, then, after the skin has dried to a large degree but is still slightly moist, applying kerosene to the skin side to neutralize the toughening action of the poke root and render the skin soft and pliable, and then drying the skin, and then washing the skin in a solvent to remove all foreign substances, glue and animal matter.

Leather-Working Machine. U. S. Patent 1,355,437. F. Wayland, Salem, Mass. Filed Apr. 22, 1920.

Hide-Stretching Device. U. S. Patent 1,355,928. F. H. Townsend, Boston, Mass. Filed Dec. 15, 1919. A device for stretching two hides simultaneously.

Leather-Flexing Machine. U. S. Patent 1,355,965. R. Hart, Milwaukee, Wis. Filed June 10, 1918. A leather flexing machine adapted for graining leather.

Machine for Scrubbing, Brushing, and Cleansing Leather. U. S. Patent 1,356,016. C. Ruhe, New York, N. Y., and F. R. Barker, Salem, Mass., assignors to Ruhe Tanning Machinery Company, Boston, Mass. Filed June 13, 1919.

Tanning Extracts. British Patent 146,165. Gerb und Farbstoffwerke H. Renner & Co., Akt.-Ges., Hamburg, Germany, assignees of H. Renner and W. Moeller. June 25, 1920. Vegetable tanning materials are decolorized and/or rendered more soluble by treatment with acid resins which are products of condensation of sulphonated hydrocarbons. The degree of solubility or decolorization attained depends on the quantity of acid resin added, *e. g.*, to obtain an extract soluble in warm water and separating only to a small extent on cooling 1 to 5 per cent. of acid resin suffices, while to obtain an extract soluble in the cold 10 to 15 per cent. is necessary. The degree of solubility and the character of the extract obtained are influenced by previous whole or partial neutralization of free sulphonic acids present in the acid resin. In practice, 1 kilogram of quebracho extract may be warmed and mixed with 100 grams of an acid resin and the mixture heated until the desired degree of solubility is obtained. As another example, 1 kilogram of liquid mangrove extract of about 22° Bé. has its dark red color lightened by warming with 50 grams of acid resin. Pressure hastens the reaction in each case.

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Tanning. British Patent 147,797. O. ROHM, Darmstadt, Germany. July 9, 1920. Skins are tanned by an iron salt solution, such as ferric chloride, to which a dilute solution of waterglass is added, any deposit of silicate of iron formed at the beginning of the process being redissolved by stirring. The skin may be placed in the iron-salt solution, and after this has penetrated the pores the desired quantity of solution of waterglass is slowly added. The action is improved by the addition of formaldehyde or other aldehydes to the bath at any desired stage; or the skins may be pickled or treated with formaldehyde before commencement of the process. In an example 100 kg. of skins are treated in a clear solution of silicate of iron prepared by adding 200-300 kg. of a 10 per cent. solution of concentrated waterglass to a solution of 10 kg. of ferric chloride in 100 liters of water. 5 kg. of common salt may be added to the ferric solution. 2-3 kg. of formaldehyde may also be added.

Leather Substitutes. British Patent 147,910. A. KORN, Levallois, Seine, France. July 9, 1920. Waste rubber and canvas tubes and tire covers are washed, surplus rubber being removed if necessary, placed in water at 100° C., flattened, boiled in water, elongated by stretching, and vulcanized. The flat bands thus obtained are then pressed and may be colored and varnished. The product is used as a substitute for leather.

Synthetic Tanning Agents. British Patent 148,126. CHEMISCHE FABRIKEN WORMS AKT.-GES., Frankfurt-on-Main, Germany. July 9, 1920. Synthetic tanning agents are prepared by coupling by means of an appropriate atom or group two different aromatic compounds, one of which is capable of coupling with diazo compounds while the other is not, and solubilizing the product by introducing acid groups during or after the coupling. According to examples:—phenol is heated with sulphuric acid, then naphthalene sulphonic acid and phosphorus pentoxide are added and the mixture heated further; cresol is sulphonated by sulphuric acid, anthracene-2-sulphonic acid is added, and then sulphur chloride, and the mixture heated; sulphur chloride is added to a mixture of phenol and naphthalene sulphonic acid and the mass heated with sulphuric acid. In a further example, a mixture of sodium phenol-*p*-sulphonate and sodium 1-naphthylamine-6-sulphonate is heated with formaldehyde solution. The products are worked up by dissolving in water, filtering, and partially neutralizing with alkali. Other condensing or coupling agents may be used, or other agents for introducing acid groups, such as chlorsulphonic acid, sodium sulphite or bisulphite or formaldehyde bisulphite. The products may be used in tanning, either alone or mixed with vegetable or mineral tanning agents.

Tanning Agents. British Patent 146,182. GERB-UND FARBSTOFFWERKE H. RENNER & CO., AKT.-GES., Hamburg. June 25, 1920. Tanning agents are prepared by treating acid resin or acid tar from mineral oil refining with chromates or bichromates or chromic acid; quinone-like bodies con-

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taining chromium are thereby obtained; any free sulphuric acid remaining in the product may be neutralized by alkali or alkaline-earth bases.

Iron Salts; Tanning Agents. British Patent 146,214. O. ROHM, Darmstadt, Germany. June 26, 1920. An iron salt having the formula $FeSO_4Cl$ and suitable for tanning is obtained by acting on ferrous sulphate either dry, crystallized or in solution, with chlorine. When crystals of ferrous sulphate are treated, a solution is first formed which on drying on a water-bath produce a crystalline cake of the composition $FeSO_4Cl_6H_2O$.

Iron Salts; Tanning Agents. British Patent 146,218. O. ROHM, Darmstadt, Germany. June 26, 1920. The compound $FeSO_4Cl_6H_2O$ which is suitable for tanning is obtained by boiling down its solution under reduced pressure, until the water content corresponds with the above formula and then cooling and, if necessary, inoculating. The solution may be obtained as described in the parent Specification or in any other manner so long as it contains iron, sulphate radical, and chlorine in the above proportions. Boiling down can be avoided by bringing together ferric chloride, ferric sulphate, and water; or ferric chloride, sulphuric acid, and water in the correct proportions, hydrochloric acid being evolved in the second case.

Synthetic Tanning Agents. British Patent 146,427. BADISCHE ANILIN- UND SODA-FABRIK, Ludwigshafen-on-Rhine, Germany. July 3, 1920. *Sulphonic Acids.*—Tanning agents are prepared by sulphonating crude anthracene, crude carbazole, or anthracene waste, and decolorizing the sulphonated product by means of chlorine, hypochlorites, oxalic acid, formaldehyde, etc.; the decolorized product is capable of giving a light-colored leather. A similar product is obtained by sulphonating the crude bodies specified above by means of chlorsulphonic acid, preferably in the presence of an inert diluent, such as nitrobenzene, at a moderate temperature; this product may be subsequently treated with decolorizing agents as above described.

Synthetic Tanning Agents. British Patent 147,534. M. MELAMID, Freiburg, Breslau, Germany. Feb. 25, 1920. *Sulphonic Acids.*—Heavy anthracene oil is sulphonated by means of concentrated sulphuric acid; the sulphonated product is diluted with water, neutralized by caustic soda, or by lime followed by caustic soda, and concentrated, and constitutes a tanning agent.

Synthetic Tanning Agents. British Patent 146,166. GERB-UND FARBSTOFFWERKE H. RENNER & Co. AKT.-GES., Hamburg, Germany, assignees of H. Renner and W. Moeller. June 25, 1920. *Sulphonic Acids.*—Tanning agents are prepared by heating hydrocarbons to a temperature below 100° C. with excess of sulphuric acid to obtain a sulphonated condensation product of resinous character; agents promoting condensation, such as formaldehyde, ketones, phosphoryl chloride, or thionyl chloride, may be added. According to examples, crude naphthalene or anthracene oil are

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heated on the water-bath with sulphuric acid until sulphonated, a little formaldehyde is then added, and the heating continued until the product solidifies to a resinous mass soluble in water. The free sulphuric acid in the product may be neutralized by an alkali or other base. The products may be used in tanning, either alone or in admixture with vegetable tanning extracts; the vegetable extracts are solubilized and decolorized by this admixture.

Synthetic Tanning Agents. British Patent 146,167. GERB-UND FARBSTOFFWERKE H. RENNER & Co. AKT.-GES., Hamburg, Germany. June 25, 1920. *Sulphonic Acids.*—Tanning agents are obtained by treating sulphonated condensation products from hydrocarbons or phenols with oxidizing agents. The products probably contain quinone groups; they are mainly insoluble in water, but can be dissolved by admixture with soluble tanning agents; this admixture may be effected by a partial oxidation of the parent substances, so that some of the soluble parent substance remains in the product.

Synthetic Tanning Agents. British Patent 146,180. GERB-UND FARBSTOFFWERKE H. RENNER & Co., AKT.-GES., Hamburg, Germany, assignees of H. Renner and W. Moeller. June 25, 1920. *Sulphonic Acids.*—Tanning agents are prepared from the waste acid resins of mineral oil refinery by adding thereto a hydrocarbon, *e. g.*, naphthalene, in amount corresponding with the sulphuric acid content of the resin and heating until a sulphonated condensation product soluble in water is obtained; agents promoting condensation, such as formaldehyde, ketones, phosphorus oxychloride, or thionyl chloride, may be added.

Tanning Agents. British Patent 146,181. GERB-UND FARBSTOFFWERKE H. RENNER & Co. AKT.-GES., Hamburg. June 25, 1920. Tanning agents are prepared by treating acid resin or acid tar from mineral oil refining with monochromates, *e. g.*, of barium, sodium, or potassium in amount equivalent to the free sulphuric acid present. Or the sulphuric acid present may be neutralized by hydroxides or carbonates of chromium, aluminium, or iron. Or the acid resin or acid tar is first treated with a monochromate, and then with an hydroxide or carbonate of chromium, aluminium, or iron.

Tanning. British Patent 144,677. BADISCHE ANILIN & SODA-FABRIK, Ludwigshafen-on-Rhine, Germany. June 9, 1920. *Extracts, Making and Treating.*—The difficulty soluble parts of tanning materials are rendered readily soluble, even in cold water, by adding to them sulphonic acids of at least tricyclic hydrocarbons, or heat condensation products of non-hydroxylated aromatic sulphonic acids either in the free state or in the form of salts thereof. In an example, 100 parts by weight of quebracho extract of about 25° Bé. are mixed with 15 parts by weight of a sodium salt of a sulphonic acid of anthracene, phenanthrene, carbazol or mixtures or raw products thereof or heat condensation products prepared there-

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from or from sulphonic acids of lower aromatic hydrocarbons such as naphthalene or toluene sulphonic acids. Other tanning extracts such as mangrove may be used in place of quebracho.

Electric Endosmose; Tanning. British Patent 146,938. ELEKTRO-OSMOSE AKT.-GES. (GRAF SCHWERIN GES.), 35, Lindenstrasse, Berlin. May 29, 1920. The process described in the parent specification is, according to the present invention, carried out with the use of a weak solution, say of density 0.1 to 0.5° Bé., during the electric tanning, which may be effected in a three-compartment cell with a pressure of 30 volts. For the subsequent non-electric tanning a liquor of density about 6° Bé. is suitable. Each step of the treatment may last 24 hours.

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REPORT OF HIDE POWDER COMMITTEE.

At a meeting of the Council of the American Leather Chemists Association held Tuesday, March 9, 1920, a Committee consisting of W. K. Alsop, H. C. Reed, C. C. Smoot, 3d, C. R. Oberfell, and F. H. Small, Chairman, was appointed to study the question of Hide Powder Supply.

The immediate reason for the appointment of this Committee was a variation which appeared between two successive batches of hide powder supplied by the manufacturer, and the object of the appointment was that a representative committee of the Association might cooperate with the manufacturer in producing a supply that would be uniform in preparation and properties, and give concordant non-tannin values when used in making tannin analyses. Only such hide powders as receive the approval of this Committee are to be accepted as official hide powder of the Association. During the last several months this Committee has cooperated with the manufacturer in a study of various methods of preparation, has agreed upon a certain method as standard, has made careful comparisons of several samples of hide powder prepared by this method, and has agreed upon a particular sample as satisfactory and comparable with the 1920 hide powder now in use. It further has authorized the manufacturer to supply the powder represented by this sample as the next official powder under the name of Official Hide Powder No. 1. This powder is now available and may be secured from the Standard Manufacturing Co., Ridgway, Pa.

Beginning with the present batch, all batches of hide powder as authorized by the Committee will be designated seriatim as Official Powders Nos. 1, 2, 3, 4, etc., the method of designation as 1919, 1920, etc., being discontinued.

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Should any member of the Association find any grave discrepancies between lots of Official Powder supplied by the manufacturer, report should be made promptly to the Chairman, giving all the particulars and accompanying with samples.

For the Committee,

F. H. SMALL, *Chairman.*

January 12, 1921.

THE ACID TITRATION OF CHROME LIQUORS.

By A. W. Thomas and S. B. Foster.

Rec'd January 11, 1921

Recent studies of the conductance titration of chrome liquors by us[1] showed that the official method for titration of chrome liquors gives low results due to the retention of adsorbed chromic sulphate in the precipitated hydrous chromic oxide.

Examination of the analysis of a pure chrome liquor made by A. W. Thomas and M. W. Kelly[2] yields further evidence concerning the failure of the official titration method to yield theoretically true results. The chrome liquor referred to was prepared by reduction of chemically pure sodium dichromate with sulphur dioxide after which the excess sulphur dioxide remaining dissolved in the liquor was completely removed. Analysis of this pure chrome liquor, containing only $Cr(OH)SO_4$ and Na_2SO_4, showed by the official methods—

(1) Cr_2O_3 ..... 242.7 gm. per liter at 25° C.
(2) Acid SO_3 ..... 251.7 gm. per liter at 25° C.
(3) Total SO_3 ..... 382.1 gm. per liter at 25° C.

The amount of $Cr(OH)SO_4$ corresponding to (1) is 527.0 grams. Deduction of the SO_3 contained in 527 grams of $Cr(OH)SO_4$ (255.6 grams SO_3) from the total SO_3 in (3) leaves 126.5 grams, which is equivalent to 224.5 grams Na_2SO_4. The ratio of moles of Na_2SO_4 to moles of $Cr(OH)SO_4$ obtained from these figures is 1 : 2.02.

Calculating the $Cr(OH)SO_4$ from (2), 518.9 grams is obtained. Deducting the 251.7 grams of acid SO_3 from (3) leaves 130.4 grams SO_3 from which the Na_2SO_4 present is indicated as 231.4

[1] This JOURNAL, 15, 510 (1920).
[2] This JOURNAL, 15, 665 (1920).

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grams. From these figures the ratio of moles of Na_2SO_4 to $Cr(OH)SO_4$ is 1 : 1.93.

Theoretically the ratio of moles Na_2SO_4 to $Cr(OH)SO_4$ in a pure chrome liquor should be 1 : 2. It will be seen that although the calculation by means of the Cr_2O_3 and total SO_3 determinations give a ratio 1 per cent. higher than this, the ratio obtained from calculations based on the determination of acid SO_3 by the official method is 3.5 per cent. lower than the theoretical value.

It is possible by means of a simple expedient to make the official method yield better results. In view of the findings of Wilson and Kern,[3] Thomas and Baldwin,[4] and of Baldwin[5] concerning the effect of neutral salts upon the actual acidity of chrome liquors, an investigation of the effect of sodium chloride on the titration of chrome liquors has been undertaken by B. B. Dhavale and S. R. Das.[6] They show that the addition of sodium chloride causes an increase in the titratable acidity. The maximum effect was found by them to be obtained when 49 grams or more of sodium chloride was dissolved in the 400 cc. of solution (containing 0.1747 gram Cr) titrated.

This has been confirmed by us and furthermore, titrations of 0.1 normal sulphuric acid, with and without salt, prove that the effect is not due to the action of salt upon the indicator; phenolphthalein. The following results are the averages of several that were obtained with chrome liquors containing 13 to 14 grams of Cr_2O_3 per liter. The volume titrated in each case was made up to 400 cc. with distilled water and the amount of 0.1 normal alkali required to give a pink color with phenolphthalein in 400 cc. of boiling distilled water, namely 0.22 cc., was subtracted from each titration. The figures are all corrected accordingly.

COMMERCIAL CHROME LIQUOR.

	Amount titrated	0.1N NaOH required	Grams acid SO_3 per 100 cc. liquor found
		(No salt)	
(1)	15 cc.	47.26 cc.	1.26
		(280 cc. 3N NaCl present)	
(2)	15 cc.	52.52 cc.	1.40
		(Conductance method)	
(3)	4 cc.	13.98 cc. 0.1 N $Ba(OH)_2$	1.40

[3] This JOURNAL, 12, 445 (1917).
[4] *Ibid.*, 12, 248 (1917).
[5] *Ibid.*, 14, 10 (1919).
[6] *J. S. L. T. C.*, 4, 225 (1920).

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PURE CHROME LIQUOR.*

		(No salt)	
(4)	15 cc.	59.04 cc.	1.57
		(280 cc. 3N NaCl present)	
(5)	15 cc.	62.51 cc.	1.67
		(Conductance method)	
(6)	4 cc.	17.12 cc. 0.1 N $Ba(OH)_2$	1.71

* Made by reduction of chemically pure sodium dichromate with sulfur dioxide.

After the end point had been reached in (4) 49 grams of sodium chloride were added which discharged the pink color. It required the further addition of 2.54 cc. of 0.1 normal alkali to restore the end point, making a total titration of 61.58 cc., equivalent to 1.64 grams of SO_3 per 100 cc. of liquor.

In our previous paper on the conductance method it was shown that this method gave results quite close to the gravimetric method for solutions of chromic sulphate. Inspection of the values submitted above shows that with the commercial liquor the titration in presence of 49 grams of NaCl (280 cc. of 3 M NaCl) gives the same value for SO_3 as the conductance method, although in the case of the pure chrome liquor, it is lower.

It appears that the official method for titrating chrome liquors can be made to yield more correct results by the addition of about 50 grams of NaCl to the solution before titration is commenced.

We take pleasure in acknowledging the generous support of Messrs. A. F. Gallun and Sons Co.

Columbia University,
New York City.

IRON TANNAGE.

By Daniel D. Jackson and Te Pang Hou.

SECTION I. GENERAL DISCUSSION.

As early as the latter half of the eighteenth century iron salts as tanning agents were proposed and experimented upon. From that time on attempt after attempt was made to obtain a satisfactory tannage with iron, but without material results. Different experimenters took up the matter with renewed enthusiasm, each cherishing a hope of thereby revolutionizing the tanning industry, but plants running on such processes were unsuccessful.

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When it is considered that next to alum, iron compounds were among the first inorganic salts introduced for mineral tannage, it may be realized how far iron tannage has fallen behind that of chrome and even of alum tannage at the present time. Diversified reasons have been given by different investigators to account for the unsatisfactory products obtained. No doubt, while some of these represent true causes responsible for the failure, much is due to a lack of understanding of the peculiar properties of the iron salts rather than to the intrinsic character of iron. It has been our object to make a study of iron tannage and to determine wherein the difficulties lie and how they may be met.

True to the general trend of the Periodic Table, aluminum with the lowest atomic weight is the most acidic, while iron having the highest atomic weight is the most basic, with chromium lying in between.[1] This accounts for some of the differences in the behavior of the three elements as tanning agents. But there seem to be, as far as the tanning properties are concerned, more fundamental differences, not in degree but in kind, which should be ascribed to their distinct properties as individual elements. For instance, both iron and alum tanned leathers do not resist boiling temperature, whereas chrome tanned leather is not affected unless it is subjected to boiling continuously for a considerable length of time.

Some investigators seem to have worked along the idea that the basic ferric sulphate corresponding to the formula $Fe(OH)SO_4$ is the compound in the liquor that brings about tanning, and have striven to produce such a basic ferric salt liquor for this purpose. This is too basic for a sulphate liquor, although ferric chloride liquor can stand a higher basicity than this. Ferric sulphate in solution corresponding to this degree of basicity is not stable and the hydrated ferric oxide, $Fe_2O_3.xH_2O$, a fine yellow crystalline precipitate, will invariably separate out within a short time, even when the liquor is not diluted. If the liquor is diluted, turbidity is almost instantaneous with a rapid separation of the light yellow precipitate. To produce a good tannage with iron, the basicity of the liquor employed is found to be considerably less than this in the case of the sulphate and the range between which the basicity may vary is rather narrow. Symbolically the

[1] See Stieglitz, "Quantitative Chemical Analysis," Vol. I, p. 195 (1919).

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salt in the ferric sulphate tan liquor may be represented by $Fe_2(OH)x(SO_4)y$ where x has a value between 1 and 1½ and y between 2½ and 2¼, but there is no definite formula assignable, as there is no sharply defined chemical compound and, besides, when it comes to neutralization, the iron that is fixed in the pelt is of a highly basic character. But any attempt to bring about the formation of such a basic salt as is represented by $Fe(OH)(SO_4)$ invariably causes a precipitate of $Fe_2O_3.xH_2O$. This $Fe_2O_3.xH_2O$ is entirely inert and we can not expect to obtain a tannage from it any more than from a precipitated $Cr_2O_3.xH_2O$ if such is produced in the chrome liquor from the use of too much alkali. The oft reported "hard and brittle leather" may be simply due to improper tannage from the presence of much precipitated $Fe_2O_3.xH_2O$. The difficulty with the iron liquor, then, is that the ferric salt, particularly the sulphate, is very readily hydrolyzed and that, what is still worse, upon hydrolysis the ferric hydroxide seems to pass through the colloidal range so rapidly that it is soon flocculated or coagulated as a light yellow crystalline substance $Fe_2O_3.xH_2O$. This will be appreciated when it is seen that $Al(OH)_3$ upon hydrolysis remains in the colloidal realm for a considerable time, and when finally separated out from the solution it does not readily become dehydrated as $Al_2O_3.xH_2O$. The same is true of $Cr(OH)_3$ from a chromic salt solution, and even more pronounced.

Another difficulty is that ferrous iron in solution, though easily partially oxidized is rather difficult to be completely oxidized. To effect a partial oxidation is one thing, but to oxidize completely all the ferrous iron in solution to the ferric state seems quite another. Oxygen from the air will partially oxidize some ferrous iron in solution to the ferric state, but it never is able to oxidize it completely, except in alkaline solution. Perchloric acid, another oxidizing agent, oxidizes iron in solution partially but complete oxidation is quite difficult. With I_2, complete oxidation is impossible, although a small amount of FeI_3 is obtained. There is normally always an equilibrium between the ferrous iron and the ferric iron in solution. To shift the equilibrium to completion requires a much higher potential which is only secured by using a powerful oxidizing agent, or for the same oxidizing agent a higher concentration of this. The equilibrium ratio is

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$$\frac{(Fe^{II})}{(Fe^{III})} = 10^{17}$$ [2]

Thus, a small concentration of ferric iron present in solution is normally sufficient to set up an equilibrium and it takes a considerable potential to shift the equilibrium to the ferric end. This consequently calls for the presence of some excess of a powerful oxidizing agent to prevent any of the ferric iron from being again reduced. Complexities result from the fact that iron is capable of existing in two different states, of which the ferric state is the one that possesses the tanning property and this gives rise to one of the great difficulties in iron tannage.

In the case of aluminum the problem is simpler, as aluminum does not exist in a state other than the trivalent, and it has little or no tendency to be flocculated into a similarly dehydrated $Al_2O_3.xH_2O$ compound in the solution.

As to chromium the condition is, on the other hand, decidedly favorable. For, while chromium does exist in other states, notably as $CrO_4^=$, or $Cr_2O_7^=$, it would take an excessively high oxidation potential to cause it to go to the chromate state, except in an alkaline solution, which is not the case with the chrome bath. Hence to all intents and purposes chromium under such conditions can be said to possess only one state of oxidation, *i. e.*, Cr^{III}, as is also the case with Al. Further, tanning conditions are far more favorable to reduction than to oxidation. The protein bodies in the hides and skins, the woody material of the drum or paddle, and the metallic joints of the apparatus all possess distinct reducing properties.. Ferric salt in the liquor which is so susceptible of reduction is always reduced to a greater or less degree, as can be easily proved by testing the spent liquor with potassium ferricyanide solution after the tanning operation. In this connection it can not be too strongly emphasized that the tan liquor should not be left in contact with a wooden or iron container unnecessarily, and should not be introduced into the drum until the tanning operation is ready to begin. Much trouble has been traced to the iron liquor being materially reduced and converted to the ferrous state during the progress of tanning. For chrome tan-

[2] See Stieglitz, "Quantitative Chemical Analysis," Vol. I, pp. 270-275 (1919).

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nage, this condition is exactly what we desire as chromium is to be kept at its lower state of oxidation, namely the chromic state.

From the above it is clear why there are added difficulties in the case of iron tannage. It is necessary, first of all, to convert the ferrous iron to the ferric state *completely,* then to keep it in this ferric state throughout the tanning operation under adverse conditions, and to prevent the separation of any hydrated ferric oxide, $Fe_2O_3.xH_2O$, by adjusting the proper acidity in the liquor employed.

Section II. History of Iron Tannage, Including Recent Work.

Attempts to use iron salts as tanning agents date back to the time when efforts were first made to find a substitute in the form of metallic salts for vegetable tannins. In the course of more than a century, efforts were repeatedly made and interest was continually revived to make iron tannage a commercial success, but without reward, in spite of the great promise that inspired such investigators to make a most determined effort. Within the last decade, partly on account of the Great War, new interest has been given to iron tannage, and the properties and behavior of iron salts as tanning agents are gradually becoming better understood.

The history of iron tannage begins from the latter part of the eighteenth century. Many of these early investigators are men who also helped to establish the present-day chrome tannage.

In the year 1770, J. Johnson,[3] an Englishman, patented a process of tanning using ferrous sulphate with an acid (sulphuric acid, hydrochloric acid or nitric acid). The pelt was tanned in three operations in the middle of which a vegetable tannin was used.

In 1794, Sam. Ashton,[4] another Englishman, recommended the use of a mixture of iron oxide and sulphuric acid, calcined iron ore or iron ochre with pyrites, copper ore, and zinc for tanning. The duration of tanning was given as from five to seven weeks. For calfskins some alumina was also added.

[3] *Handbuch der Chromgerbung,* Josef Jettmar, p. 133 (1900); also *Die Chromgerbung,* J. Borgmann, p. 6 (1902).

[4] *Ibid.*

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In 1805, Sigmond Hermbstadt[5] in his book on leather tanning explained that solutions of metallic acid baths had similar action on the pelt as the oak tannins. Among other salts he mentioned the red iron sulphate, in which not only the grain of the pelt was affected, but the pelt was virtually converted into leather if soaked in it for some time. He prepared his iron tan liquor by heating ferrous sulphate to a dry yellow substance which was dissolved in twenty times its volume of boiling water, and on cooling, the clear yellow-red solution decanted for use. He also treated iron oxide with acetic acid, or oxidized ferrous sulphate with concentrated nitric acid or with a mixture of concentrated nitric acid and sulphuric acid. Sole leather as well as upper leather could be made in this way but the leather obtained was detanned in contact with water.

In 1842, d'Arcet,[6] a Frenchman, tanned the hides in a ferric sulphate solution but the sulphuric acid set free gradually destroyed the hides. In the same year, Julius Bordier,[7] of London, patented a process (British Patent 9,219, 1942) of oxidizing ferrous sulphate with nitric acid and sulphuric acid, and with manganese dioxide and sulphuric acid. It was said that he had attained some success.

In 1853, Hylten Cavalin,[8] employed for tanning, liquor containing 10 pounds of dichromate of potash and 20 pounds of alum in 180 pounds of water. The hides were tanned in this liquor for four days, and were next placed in a 10 per cent. ferrous sulphate solution for twelve hours with frequent stirring. The acidity relation of these two liquors was not properly adjusted and the iron was not completely oxidized. The leather obtained was hard and brittle.

In 1855, Rene de Kercado Molac and Jean Daniel Friedel,[9] both of Strasbourg, France, patented a process whereby the hides were tanned in a basic ferric sulphate solution which was later neutralized with metallic oxides, such as ferric oxide, alumina,

[5] "Le Tannage au Fer," *Le Cuir*, Josef Jettmar, June 15, 1919.

[6] "Leather Industry," A. M. Villon, trans. by F. T. Addyman, p. 189 (1901).

[7] See also "The Arts of Tanning," Campbell Morfit, p. 396 (1852).

[8] "The Arts of Tanning," Campbell Morfit, pp. 397-401 (1852).

[9] Compare "Handbuch der Chromgerbung," Jettmar, p. 137.

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and zinc oxide to remove the sulphuric acid liberated. They prepared the liquor with ferrous sulphate, manganese dioxide and sulphuric acid, and added to the liquor ferric acetate in varying proportions. A. E. L. Bellford, of London, patented their process in England. In this British patent (January 12, 1855) it was stated that the leather treated by other mineral processes is "liable to tear in length of time on account of the great quantity of acid remaining in the leather corroding the animal fibres."

Dr. Frederich L. Knapp, Professor of the Polytechnic School of Brunswick, Germany, made a thorough, scientific investigation on these mineral tannages and published the results in "Die Natur und das Wesen der Gerberei und des Leders" (Munich, 1858), and also in an article, "Über Gerberei und Leder," in Dingler's Polytechnische Journal, Vol. 181, p. 311 (1866). He made a satisfactory explanation of the tanning action. He had in mind the possibility of reducing the length of time needed in the vegetable tanning process and eliminating the costly materials such as egg-yolk and flour used in alum tannage. He recognized the plumping effect upon the hides by the acid liberated during tanning and the stiff and brittle character of the leather obtained. He recommended neutralizing the tan liquor during the progress of tanning with sodium carbonate or caustic soda and pointed out the advantages in so doing, namely, that the hides were more richly tanned, that the harmful acid effect was prevented, and that a neutral electrolyte NaCl (in $FeCl_3$ liquor) was produced in the tan liquor. His English patent (British Patent 2,716, 1861, through John H. Johnson) covered iron, chrome, manganese, and other metallic salts in combination with fatty acids to form insoluble metallic soaps so that the iron in the pelt might not be washed out. He also mentioned the use of similarly insoluble silicates of aluminum and alkaline earths. According to his patent (German Patent No. 444, 1877) he prepared his liquor by adding nitric acid in excess to oxidize completely a boiling ferrous sulphate solution when brown nitrogen dioxide (NO_2) fumes were seen. After all iron was oxidized he introduced more ferrous sulphate into the resulting solution as long as NO_2 fumes were evolved. The liquor after evaporation becomes a varnish-like liquid. Judging from this description his liquor must have been too alkaline through the loss of the nitric acid by boiling. In his additional patent

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(German patent No. 10,518, 1879) he used instead of the nitric acid, sodium nitrate and sulphuric acid for oxidation. This method is far more economical and involves no danger of losing the acid by heating so that the acidity of the resulting liquor is under control. Furthermore, a neutral salt, Na_2SO_4, is produced in the tan liquor.

In 1864, F. Pfannhauser[10] obtained a patent for the preparation of a basic ferric sulphate solution and its use in tanning. He roasted ferric sulphate to a red heat with continuous stirring until it was reduced to a red powder which was then thrown into water while still hot. Most of this powder was said to be dissolved. The suspension was allowed to settle and the supernatant liquid drawn off for the preparation of tan liquors of varying strength. The skins were tanned countercurrently and, when tanned, placed in a soap solution.

In 1877 Paesi[11] proposed to use a ferric chloride solution together with salt at 20° C. in the ratio of 100 parts of water to ten parts of $FeCl_3$ and five parts of salt.

In 1881, E. Harcke obtained a German patent, No. 19,633, according to which the pelt for making sole leather was treated with a mixture of a resinous body (such as rosin), coal tar creosote, or carbolic acid, and an alkali, in water, until thoroughly penetrated. The pelt was then tanned, first in an aluminum salt solution and then in a ferric chloride solution, or other ferric salt solution. For making upper leather the hides were previously limed and if softness and porosity were desired, the rosin could be omitted.

In 1881, W. Eitner[12] patented a process (Austrian Patent No. 6,775) using a mixture of a basic chromic sulphate and ferric sulphate solution. This process was used in Graz, Austria, and the product known as "Patentleder, Marke Elefant." By changing the ratio of the chromic salt to the ferric salt different gradations of color—from yellow (of the iron) to gray (of the mixture) and to green (of the pure chrome)—were obtained. When a mixture of the ferric and chromic salts was used, the leather was colored black with logwood alone; when chromic salt alone

[10] "Manufacture of Leather," Chas. T. Davis, p. 290 (1897).

[11] "Leather Industry," A. M. Villon, trans. by Addyman, p. 189 (1901).

[12] "Die Chromgerbung," J. Borgmann, pp. 49-54 (1902); also "Handbuch der Chromgerbung," Jettmar, p. 151 (1900).

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was used, the leather was colored black with logwood and an iron "striker." When yellow color was not desired in the product, chromic salt alone was used for tanning. Leather obtained in this way was stuffed, after sammying, with mixtures of train oil, castor oil, stearin, tallow, mineral oil, etc., with soda bicarbonate, soap, borax, casein, etc., as emulsifying agents.

In 1886, John W. Fries, of Salem, North Carolina, patented a process of tanning (U. S. Patents Nos. 343,166 and 343,167) using ferrous carbonate (or ferrous sulphate), sodium carbonate (or sodium bicarbonate) and sulphuric acid. The skins were tanned first in a dilute liquor for two or three days and then in a more concentrated liquor for the same length of time. A small amount of sugar might be added. After the tanning operation the skins were hung in the air to get the iron oxidized. For currying, he used tallow with a paraffin oil, lard, or cotton seed oil, and later, in his patent No. 343,167, he recommended an alcoholic solution of castor oil.

In 1892, Paul F. Reinsch, Erlangen, Bavaria, patented a process (German Patent No. 70,226) using a liquor prepared by mixing 10 kg. $FeCl_3$ dissolved in 40 l. of water with 4½ kg. crystalline Na_2CO_3 dissolved in 20 l. of water, thus yielding a dark brown solution. He called it ferric chloride-sodium chloride liquor, which he used for making different kinds of leather either alone or in combination with alum-sodium chloride tannage. In 1912 he obtained another German patent, No. 265,914, on the use of ferric chloride and magnesium carbonate. He prepared the liquor by dissolving 1 kg. ferric chloride in 4 l. of water to which was added a suspension of 225 g. $MgCO_3$ in a liter of water. To this mixture he added a solution of 8 per cent. aluminum chloride. Evidently his idea is to bring about the required basicity by $MgCO_3$. The $AlCl_3$ present is probably meant to help keep the basic ferric chloride in solution.

J. Bystron and Karl Baron von Vietinghoff obtained a number of German patents, Nos. 255,320, et seq., in 1911, a British patent, No. 13,952 in 1912, and two U. S. patents, No. 1,048,294 in 1912 and No. 1,061,597 in 1913. They employ nitrogen dioxide, NO_2, and nitrogen trioxide, N_2O_3, for the oxidation of iron. The nitric oxide, NO, from the oxidation reaction is collected and reoxidized by contact with fresh air to NO_2 and N_2O_3, which gases are used

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over again for oxidation. They thus proposed to utilize the NO_2—NO—NO_2 cycle, making the oxides of nitrogen virtually catalytic agents for the oxidation of iron. In the British patent, No. 13,952, they observed considerable precipitates formed in the tan liquor and on the skin. According to them, the presence of large quantities of an acid causes the formation of a highly acid and not completely insoluble iron oxide in the skin so that the leather made is brittle and can not be stored. In this patent and also in the U. S. patent No. 1,048,294 he proposed placing the skin in a ferrous salt solution and oxidizing the ferrous iron by passing in NO_2 gas from outside or by liberating HNO_2 from a nitrite added to the liquor. Thus they attempt to combine the oxidation reaction and the tanning operation in a single procedure. It is true that HNO_2 (from a nitrite and an acid) has sufficiently high oxidation potential to oxidize ferrous iron to the ferric state, but in order to oxidize all the ferrous iron into the ferric state completely, the presence of much acid in the solution and of an excess of the oxidizing agent is needed. If the oxidation by HNO_2 or oxides of nitrogen is to take place simultaneously with tanning operation at the low acidity necessarily present in the tan liquor, probably there will be much difficulty in getting all of the ferrous iron completely oxidized. Bystron in the U. S. patent No. 1,061,597 patented the use of a neutral alkali salt such as Na_2SO_4 or NaCl for treating the iron-tanned leather. He claimed that by this treatment a more insoluble basic ferric salt of a light color is formed in the leather, thereby yielding a soft, elastic, and non-brittle leather.

O. Röhm in 1917 obtained British patents Nos. 103,827 and 104,338 on the combination tannage using formaldehyde and ferric chloride, or formaldehyde and a mixture of ferric chloride and chromic chloride or aluminum chloride. In his patent No. 103,295 (not accepted) he mentioned the use of ferric alum mixed with vegetable tannins to form iron tannate (ink) for tanning. In his patent No. 103,827 he recommended tanning with formaldehyde in sodium bicarbonate solution followed by a tannage with a ferric chloride solution, a mixture of ferric chloride and chromic chloride, a mixture of ferric chloride and aluminum chloride, a ferric chloride solution and then vegetable tannins, or a ferric chloride solution with an alkaline sulphide. He also mentioned

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the treatment of the skin with an iron precipitant, such as NH_3, alkalies, or alkaline salts; or phenols, naphthols, organic carboxylic acids, vegetable tannins; or soap, sulphide, polysulphide, and the like. He mentioned that the leather obtained would not become slippery in wet condition as is the case with a chrome leather. In his patent No. 104,338 he stated that the aldehyde tannage could be advantageously used to follow iron tannage after neutralization or together with neutralization. When the aldehyde is introduced together with the neutralization after the iron tannage, there is, according to his observation, an advantage that the grain-drawing so common in a mineral tannage will be prevented. His thought seems to be along the line that since aldehyde tannage is carried on in an alkaline solution, the introduction of the aldehyde tannage after the iron will serve also as a neutralization operation to fix the iron in the pelt. We have tested this combination tannage and found the leather so obtained satisfactory. But since formaldehyde is a tanning agent by itself, to what extent the iron salt has contributed to the tannage is difficult to tell.

Emil Kanet[13] in his German patent No. 306,015 (1918) introduced an interesting feature in the mode of tannage. He derived the tanning action by the hydrolysis of a ferric salt. He treated the pelt at a low temperature with a ferric salt solution of such a basicity that it would be unstable at the ordinary temperature, and, after allowing the liquor to penetrate the pelt, raised the temperature to bring about hydrolysis. To illustrate, he placed the skins in a basic ferric acetate liquor containing from ½ to 2½ per cent. Fe_2O_3, preferably with the addition of some salt or other electrolyte such as sodium acetate. After the skins were penetrated by the tanning liquor he transferred them to a fairly concentrated salt solution at a temperature of from 45° to 60° C., or exposed them to heat in a warm chamber. The tanning action was completed in a short time but the stock was further laid aside for some time to fix the iron. The acetic acid set free under the influence of heat can be recovered from the skins by pressure. If a filling material such as flour is used with the tan liquor, it is, according to him, fixed in the leather with the basic

[13] Compare also "Le Tannage au Fer," by J. Jettmar, *Le Cuir*, July 1, 1919.

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ferric acetate. Other mineral salts such as chromic salt can be mixed with the iron. The advantage claimed is that at a low temperature a more basic ferric salt solution can be used and that the oxidizing activity of the ferric iron towards the skins is lessened.

W. Mensing in his Swiss patent No. 75,775 in 1918, recognized the ease with which ferric salt in solution is decomposed and mentioned the effect of ferrous iron upon the skin when the ferrous salt is present in the tan liquor. He recommended the use of an excess of an oxidizing agent and patented the use of a chlorate (Na, K, or Ba) as the oxidizing agent. He also recommended a preliminary treatment of the skin with borax or a basic aluminum or chromic salt solution for the use of a slightly more acid or neutral ferric liquor. According to his idea the tanned stock should not be washed with water but only wrung or pressed to get rid of the excess of the tan liquor. On drying, the stock is oiled with a mineral oil, paraffin or ceresin and then washed. To avoid reaction of the iron in the pelt with vegetable tannins he recommended fixing the iron by treating the leather with a slightly alkaline solution before vegetable retanning. He advocated the bleaching of the leather by detanning the surface layers by means of a reducing agent and then an acid. On the whole, his patent marks a better understanding of the properties of the iron tan liquor and the process of iron tannage.

Vittorio Casaburi,[14] in the articles, "Notes on the Tannage of Skins with Iron Salts," published the results from a series of his experiments, using a basic ferric sulphate solution (from the oxidation of ferrous sulphate with a mixture of nitric acid and sulphuric acid), a solution of a mixture of basic ferric chloride and sulphate (from the oxidation of ferrous sulphate by nitric acid and hydrochloric acid), a basic ferric chloride solution, and a basic ferric acetate solution. He employed a strength of iron liquor containing 1 per cent. Fe_2O_3 of the weight of the pelt in a little over four times the weight of water of the weight of the pelt. According to him 7.88 per cent. of Fe_2O_3 in the leather on the basis of the dry weight is sufficient to convert the pelt into leather. He stated that he had started with a tan liquor having such a basicity as to correspond to the formula $Fe_2(SO_4)_2(OH)_2$,

[14] *Le Cuir*, Aug. 1, Sept. 1 and Sept. 15, 1919.

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but his iron and basicity determinations in the liquor showed that the liquor he used was more acid than this, the basicity of his first liquor (basic ferric sulphate) being only one-half of this value, and that of his second liquor (a mixture of basic ferric sulphate and chloride) less than a half of this value. We have found that a sulphate liquor having so high a basicity as to correspond to $Fe_2(SO_4)_2(OH)_2$ is too alkaline for use. Throughout the course of tanning he strengthened the liquor with fresh portions of the strong liquor. He drew a conclusion that the final basicity of the liquor was the same as that at the beginning of tanning—a conclusion that has not been confirmed by our experiments. (To be continued.)

NATURE OF HIDE-TANNIN COMPOUND AND ITS BEARING UPON TANNIN ANALYSIS.*

By John Arthur Wilson and Erwin J. Kern.

In an earlier paper[1] the authors described a new method of tannin analysis which they believe gives the true tanning value of vegetable materials. Comparative tests showed the official method of the American Leather Chemists' Association to be greatly in error, exceeding 200 per cent. for typical samples of gambier extract. (The earlier paper should be referred to for a working description of both methods.) The much higher percentages of tannin obtained by the A. L. C. A. method for every material examined were attributed to the formation of readily hydrolyzable compounds between the hide powder and a variable fraction of the non-tannins. At the 17th annual meeting[2] of the A. L. C. A. a formal discussion[3] of this paper was staged, and the chief aim of the opposition was apparently to show that the low results obtained by the new method were due to losses of tannin in the manipulation. It was contended that a certain proportion of the tannin of a liquor will form a stable compound with hide only after long contact, and, further, that even tannin which has already combined with the hide will be removed to an appreciable

* Reprinted from *J. I. and E. C.*, 12, 1149 (1920).

[1] "The True Tanning Value of Vegetable Tanning Materials," This Jour., 15, 295 (1920).

[2] Atlantic City, N. J., May 27 to 29, 1920.

[3] Printed in full, This Jour., 15, 451 (1920).

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extent during the washing required by the new method; but no really conclusive evidence was offered in support of these contentions. The object of the present work was to investigate these points because they are of great importance, not only to the new method, but to the theory and practice of tanning itself.

Tanning Materials Examined.

Certain differences in behavior of the several different tanning materials have caused a widespread belief that some tannins form more stable compounds with hide than others; for example, the tannin from gambier is supposed to form a compound with hide less stable than that from hemlock bark. It has also been supposed that mixtures of tanning materials behave differently in this respect from the individual materials. We have therefore chosen for examination typical commercial tanning extracts ranging in properties from the extremes of gambier and sumac to those of hemlock and quebracho, and have also included two mixtures, each consisting of a pair of extracts of very different nature. The analyses of the eight extracts and two mixtures, both by the new method and by the official method of the American Leather Chemists' Association, are given in Table I, along with the percentage errors involved in the A. L. C. A. method, assuming that the new method is correct.

TABLE I.—Comparative Analyses of Extracts Studied, by New Method and by the A. L. C. A. Method.

	Percentage analysis of material—A. L. C. A. Method					
		Insoluble	Soluble matter		New	Per centage error in
Extract	Water	matter	Non-tannin	Tannin	method tannin	A. L. C. A. method
Quebracho	22.28	9.61	7.24	60.87	46.84	30
Gambier	50.17	7.43	16.79	25.61	7.87	225
Quebracho-gambier mixture	44.53	7.39	14.86	33.22	20.67	61
Oak bark	52.43	3.10	18.28	26.19	15.52	69
Chestnut wood	52.47	3.64	18.19	25.70	13.99	84
Hemlock bark	56.10	6.23	10.99	26.68	23.47	14
Chestnut wood hemlock bark mixture	53.89	5.94	14.53	25.64	18.73	37
Larch bark	51.26	7.42	18.36	22.96	11.29	103
Sumac	51.24	1.01	22.24	25.51	16.36	56
Wattle bark	50.20	1.50	14.75	33.55	24.66	36

It is interesting to compare the errors found for the sumac and hemlock bark extracts with those for the actual leaves and bark noted in the earlier paper. Extract manufacturers often remove

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only about 80 per cent. of the tannin from the raw materials, because in order to get the last 20 per cent. they would have to extract a large proportion of undesirable non-tannins that would considerably lower the purity of their products. The raw materials used were extracted completely and therefore contained a higher ratio of non-tannin to tannin than the commercial extract, and this, as the authors have shown, increases the error obtained by the A. L. C. A. method.

Resistance of Leather to Washing.

Three methods of measuring possible losses of combined tannin during the washing of leather were considered. The first was to wash the leather free from soluble matter and analyze it for tannin, and then to wash it further and analyze it again. The second was to use the gelatin-salt reagent (10 g. gelatin plus 100 g. NaCl per liter) in testing the wash waters for tannin; provided all tests were negative; it would show that only a very small amount of tannin, if any, was washed out. The third was to collect and weigh the soluble residues from a number of wash waters. Of these, the first method appeared most important and consequently received greatest attention.

TABLE II.—Showing Effect of Excessive Washing of the Tanned Hide Powder upon the Per cent. of Tannin Found by the New Method.

Extract	Extract grams in 200 cc. soln.	Hide substance in powder used to detannize 200 cc. soln. grams	Per cent. tannin in extract. Value obtained from analysis of tanned powder washed		
			15 times	25 times	50 times
Quebracho	3.80	10.44	46.84	47.25	46.90
Gambier	10.00	10.44	7.87	7.89	7.67
Quebracho-gambier mixture *	6.90	10.44	20.67	20.34	20.43
Oak bark	13.60	10.40	15.52	15.36	15.35
Chestnut wood	13.60	10.32	—— ‡	13.99	13.93
Hemlock bark	13.00	10.32	23.47	23.38	23.50
Chestnut wood-hemlock bark mixture †	13.30	10.32	—— ‡	18.73	19.05
Larch bark	13.60	10.32	—— ‡	11.29	11.28
Sumac	13.00	10.39	16.36	16.29	16.39
Wattle bark	8.00	10.32	24.66	24.16	24.73

* Mixture of 19 parts solid quebracho extract to 50 of gambier extract.

† Mixture of 68 parts of chestnut wood extract to 65 of hemlock bark extract.

‡ Calculation not made because 15th wash water gave test for non-tannin with ferric chloride.

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Procedure and Results.—Portions of all 10 samples were dissolved in water to give the concentrations noted in Table II. For each sample 12 g. of air-dry hide powder, of known hide-substance content, were put into each of five wide-mouth, half-pint bottles, 200 cc. of tan liquor were added to each, and the bottles stoppered and shaken in a rotating box for six hours. At the end of this time all solutions gave a negative test for tannin with the gelatin-salt reagent. The bulk of detannized liquor was removed from each powder by squeezing through a suitable cloth. Two powders from each set were allowed to dry slowly, without previous washing, and bottled for use in connection with an investigation of the "aging" of leather to be mentioned later. The remaining three powders of each set were washed as follows: Each powder was returned to its bottle along with 200 cc. water and shaken for an hour. The aqueous extract was separated from the powder by squeezing through a cloth, and the washing operation was repeated. Of the three powders of each set, one was washed fifteen times, the second twenty-five times, and the third fifty times. After washing, the tanned powders were allowed to dry slowly, and were then analyzed for water, ash, fat (chloroform extract), and hide substance (nitrogen $\times$ 5.62). The per cent. of tannin was calculated by difference. The results are given in Table II.

The detannized liquor and fifteen wash waters from one of the gambier samples were evaporated separately to show the rate at which the soluble matter is removed by washing. Table III shows that only 12 mg. of soluble matter were removed by the fifteenth wash water, which appeared colorless and gave no color upon addition of a drop of ferric chloride solution. The smallness of the weights of the residues made the evaporation of individual wash waters beyond the fifteenth of doubtful value. However, all wash waters from the twenty-sixth to the fiftieth (5,000 cc. in all) were collected from both the sumac-tanned and larch-tanned powders, and evaporated to dryness. The total matter extracted from the former was only 67 mg., and from the latter only 51 mg. Pure hide powder washed in the same way was found to yield even greater residues because of slow hydrolysis, and it should be remembered that hide powder was used in great excess in these tests. If the 67-mg. residues from the sumac-tanned

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powder consisted solely of hide substance, it would contain 12 mg. of nitrogen; a Kjeldahl determination gave 14 mg. Furthermore, the residues from the tanned powders resembled those from pure hide substance in odor and general appearance.

TABLE III.—SHOWING SPEED OF WASHING OF POWDERS TANNED WITH GAMBIER.

Soluble residue from	Weight mg.
Original detannized solution	1408
1st wash water	776
2nd wash water	396
3rd wash water	250
4th wash water	160
5th wash water	101
6th wash water	68
7th wash water	45
8th wash water	33
9th wash water	31
10th wash water	22
11th wash water	17
12th wash water	16
13th wash water	13
14th wash water	12
15th wash water	12

All wash waters without exception gave negative tests with the gelatin-salt reagent. Baldracco and Camilla[4] recently proposed a reagent for which they claimed greater sensitivity than the gelatin-salt reagent. Their reagent was made by dissolving 0.9 g. gelatin in 50 cc. water and adding 10 cc. glacial acetic acid. While this solution appears to be more sensitive than a gelatin-salt solution which has been kept for some weeks, we found it much less sensitive than the gelatin-salt reagent immediately after preparation. When the gambier liquor was diluted 100 times and a drop of freshly prepared gelatin-salt reagent was added, a distinct precipitate was formed, whereas a freshly prepared gelatin-acetic acid reagent gave a negative test. We found that the gelatin-salt reagent must be prepared from the highest quality gelatin and used only on the day it was made for the most satisfactory results. The gambier liquor had to be diluted 200 times before it failed to give a test, and all the other liquors even more. Since no tests were obtained for any wash waters, at the end of fifteen washings

[4] *J. S. L. T. C.*, 4, 101 (1920); Abst. This JOUR., 15, 545 (1920).

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not more than 8 per cent. of the tannin originally present in the tan liquor could have been removed by washing. In other words, even if, as is most unlikely, each wash water removed an amount of tannin that would just fail to give a test with the gelatin-salt reagent, we should have to increase the per cent. of tannin found for gambier extract, the material least sensitive to the test, only from 7.87 to 8.55, whereas a figure of 25.61 is obtained by the A. L. C. A. method.

Conclusions.—The results show conclusively that prolonged washing is quite without influence upon the values obtained for the per cent. of tannin in various materials by the new method, and, further, that tannin once combined with hide cannot be washed out by any amount of washing that would be practical. Thus the major contention of opponents of the new method is disproved.

Another Valuable Property of Certain Non-Tannins Not Before Fully Recognized.

In our earlier paper it was shown that non-tannins like gallic acid are valuable agents in rendering too astringent tan liquors sufficiently mild for practical use. We now find that these same non-tannins are capable of undergoing chemical change with the formation of substances capable of tanning. During his criticism of the new method, G. W. Schultz[5] said: "We have taken the non-tannins and washings and reconcentrated them under a high vacuum to the original volume of 200 cc. and have tanned hide powder with it, and, by the calculations employed, we have found a definite percentage of tannin." He mentioned also that the concentrated liquor gave a positive test for tannin with the gelatin-salt reagent. It might look at first sight as though the detannized liquor and wash waters, before concentrating, really had contained tannin and Schultz evidently so regarded it. This view, however, would be difficult to reconcile with the experimental data noted in the preceding section. We confirmed Schultz's findings while analyzing a sample of gambier extract by the new method. The detannized liquor and 15 wash waters, all of which gave no test with the gelatin-salt reagent, were concentrated to 200 cc., whereupon they were found to give a bulky precipitate with the reagent.

[5] This Jour., 15, 455 (1920).

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But, when diluted back to 3,200 cc., they still gave a bulky precipitate with the gelatin-salt reagent, showing that a most important chemical change had taken place during the concentrating.

TABLE IV.—GAMBIER EXTRACT.

200 cc. solution containing 9.00 g. extract were detannized with 12 g. air-dry hide powder, containing 10.40 g. hide substance, and then the tanned powder was washed 17 times with 3,400 cc. water. The residual liquor and wash waters were evaporated to 250 cc. and used to tan 12 g. fresh hide powder, which was afterwards washed as usual.

Total tannin either originally present or formed during the concentrating of the wash waters, 13.50 per cent.

Analysis of air-dry leather	Hide powder tanned in: Original solution	Hide powder tanned in: Concentrated wash waters
Water	17.31	16.24
Ash	0.16	0.14
Fat	0.39	0.42
Hide substance (N × 5.62)	76.86	79.38
Tannin (by difference)	5.28	3.82
Per 100 g. hide substance:		
Tannin found, grams	6.87	4.81
Material used, grams	86.54	86.54
Per cent. tannin in extract	7.94	5.56

Another sample of gambier was analyzed by the new method and found to contain 7.94 per cent. tannin. The detannized liquor and 17 wash waters (3,600 cc. in all) were evaporated to 250 cc., analyzed by the new method, and found to contain 5.56 parts of tannin per 100 of original extract, giving the extract a total of 13.50 per cent. tannin. The detailed results are given in Table IV. In order to show that this increased amount of tannin would have combined with the hide powder had it been present in the original solution, we made up a new solution of this extract, concentrated and diluted back several times, and then analyzed it by the new method, finding 12.69 per cent. of tannin. If the concentrating had been continued a little longer the figure 13.50 would probably have been reached or passed. The results are given in Table V.

In spite of the great change in the tan liquor produced by concentrating, it is not shown to any appreciable extent in the analyses by the A. L. C. A. method shown in Table VI. Concentrating the tan liquor and diluting back caused a rise in per cent. of tannin by the new method from 7.94 to 12.69, but the rise in the A. L. C. A. method is only from 26.14 to 26.40, which difference is so

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TABLE V.—GAMBIER EXTRACT.

(Same as noted in preceding table.)

Dissolved 60.00 g. extract in 1 liter of water. Concentrated to 250 cc., and diluted back to 1 liter. Repeated 3 times, the fourth time diluting to 2 liters. 200 cc. diluted solution containing 6.00 g. original extract were detannized with 12 g. air-dry hide powder, containing 10.37 g. hide substance, which was afterwards washed as usual.

Analysis of Air-Dry Leather.

Water	18.23
Ash	0.18
Fat	0.42
Hide substance (N × 5.62)	75.62
Tannin (by difference)	5.55
Per 100 g. hide substance:	
Tannin found, grams	7.34
Material used, grams	57.86
Per cent. tannin in extract	12.69

small as even to be attributable to experimental error. The reason for this small difference is probably that the non-tannins which are convertible into tannin all combine with the hide initially, even though they are easily removed later by washing.

TABLE VI.—GAMBIER EXTRACT.

Both the original liquor noted in Table IV and the specially treated liquor noted in Table V were appropriately diluted and analyzed by the A. L. C. A. method.

	Per cent. of original extract	
	Original liquor	Treated liquor
Insoluble matter	7.66	8.62
Non-tannin	18.33	17.57
Tannin	26.14	26.40

Just what chemical actions are involved in the conversion of non-tannin to tannin must remain a matter of speculation until more data are available; oxidation, condensation, and polymerization may all be involved. It is conceivable that gallic acid might be converted into digallic acid under suitable conditions, and it seems extremely likely that a polymerized form of digallic acid would have tanning properties. A solution of pure gallic acid gives no test for tannin, but after boiling for some time it gives a bulky precipitate with the gelatin-salt reagent, and apparently will tan hide. A detannized solution which gives no test for tannin can be made to give a strong test merely by passing oxygen

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gas through it. Long exposure to air has a similar action. It is evident that the new method furnishes a valuable means of studying the conversion of non-tannins into tannin, and might conceivably be applied to a study of the formation of tannins in nature and to the aging of barks.

THE TIME FACTOR IN TANNING AND THE "AGING" OF LEATHER.

The results of the preceding section suggest that the conversion of non-tannin into tannin is responsible for two factors of great importance to tanners of heavy leather, namely, the time factor in tanning and the "aging" of leather. In the discussion referred to, Alsop[6] remarked that sole leather tanned slowly not only contains more tannin, but actually consumes less tanning material than the rapid tannages. In a private communication, Professor Procter, of Leeds, has called attention to the fact that leather stored for a long time, or "aged," before washing contains more tannin than if it had been washed immediately after tanning. The extent of this aging is well shown in the following experiment:

TABLE VII.—EFFECT OF "AGING" UPON PER CENT. OF COMBINED TANNIN IN LEATHER.

Two 12-g. portions of hide powder were used to detannize 200-cc. portions of the solutions of tanning materials noted in Table II. One portion in each case was washed 25 times immediately after tanning; the other portion was allowed to dry without washing. kept exactly 30 days, and then washed 25 times.

Extract	Tannin as per cent. of original extract	
	In leather washed immediately after tanning	In leather kept 30 days before washing
Quebracho	47.25	53.00
Gambier	7.89	10.49
Quebracho-gambier mixture	20.34	23.92
Oak bark	15.36	17.23
Chestnut wood	13.99	18.02
Hemlock bark	23.38	24.87
Chestnut wood-hemlock bark mixture	18.73	20.45
Larch bark	11.29	13.22
Sumac	16.29	17.94
Wattle bark	24.16	25.89

In the work of the resistance of leather to washing, we tanned five portions of hide powder with each sample of tanning material

[6] *Loc. cit.*, p. 464.

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examined, of which three were washed immediately after tanning and two dried without washing. After thirty days the washing of one of these powders from each set was begun. After the twenty-fifth washing it was dried and analyzed for comparison with the powders washed immediately after tanning. The results in Table VII show a distinct increase in tannin due to aging. It is intended to keep the fifth powder of each set for a full year before washing.

Suitability of the New Method as a Standard.

We believe that the experimental data in this and the earlier paper prove not only that the new method is correct, but that the A. L. C. A. method, and, therefore, also the official methods of Europe, are greatly in error. In actual practice we found barely 50 per cent. as much tannin in the leather coming from a certain upper leather yard during a 3-year period as was put into it, according to the analysis by the A. L. C. A. method of the extracts used. On the other hand, the new method now checks this yard easily within the limits of experimental error. We feel justified in recommending that the new method, or some modification of it, be adopted as a standard to replace the present official methods.

It has been contended, and perhaps rightly, that the new method is so time-consuming as to make it unpopular for routine work, but it should be realized that no serious effort has yet been made to simplify the method, all work up to the present time having been confined almost exclusively to the question of correctness. One modification that appears promising for routine control work is to tan the hide powder as usual, transfer it to an alundum thimble, wash it by means of a mechanical arrangement, and then dry and weigh it, the increase in weight of the dry hide powder being taken as tannin. No doubt other modifications will suggest themselves as the work proceeds, but the saving of time is not sufficient compensation for the errors involved in the official methods.

Summary.

Tannin once combined with hide cannot be removed to an appreciable extent by any amount of washing that would be practical.

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It has been discovered that chemical changes are produced in a tan liquor by boiling or exaporating, whereby certain non-tannins are converted into substances capable of tanning. Such changes can be followed quantitatively by means of the authors' new method for tannin analysis, but not by the official method of the American Leather Chemists' Association. The new method can also be used to study the "aging" of leather.

The new method gives results which agree closely with tanning practice, whereas the A. L. C. A. method was found to be greatly in error.

It is recommended that the new method be adopted as a standard.

THE CAUSTIC ALKALINITY OF LIME LIQUORS. COMMITTEE ON LIMEYARD CONTROL. IV.*

By William R. Atkin and John Atkin.

In a recent publication[1] by one of us, a method was described for ascertaining the caustic alkalinity of lime liquors but the method so described was indirect and involved four separate determinations. We have present in lime liquors the following substances which constitute alkalinity:

(*a*) Calcium hydroxide.
(*b*) Sodium hydroxide.
(*c*) Sulphydrates of sodium and calcium.
(*d*) Ammonia and perhaps amines but these latter are present, if at all, in very small amounts and may be ignored for practical purposes.
(*e*) Sodium and calcium salts of the various protein decomposition products such as proteoses, peptones, amino acids and fatty acids produced from amino acids by deaminisation.

In order to maintain uniformity with the previous paper the letters (*a*), (*b*), (*c*), (*d*) and (*e*), are employed to refer to calcium hydroxide, sodium hydroxide, etc., as above, so that $a + b$ is the caustic alkalinity. In addition all estimations are per-

* Reprinted from *J. S. L. T. C.*, 4, 236 (1920).

[1] W. R. Atkin and W. E. Palmer, *J. S. L. T. C.*, 111, 1920.

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formed on 25 cc. portions of the filtered lime liquor and results stated in cc. N/10 acid or alkali.

Several methods have been suggested for ascertaining the caustic alkalinity directly by one titration but they proved of little value owing to the difficulty of choosing a suitable indicator.

We have in lime liquors two strong bases, sodium and calcium hydroxides, together with a weak base, ammonium hydroxide and the salt of a strong base combined with a weak acid (sodium sulphydrate which is formed from the sodium sulphide used for sharpening the lime liquors). It is well known that indicators such as phenolphthalein which have a color change on the alkaline side of true neutrality cannot be used for the accurate titration of ammonia solutions. On the other hand an indicator such as methyl orange which possesses a color change well on the acid side of true neutrality would cause to be included in the titration not only the caustic alkalinity but all the ammonia, hydrosulphide, and also the sodium and calcium salts of the decomposition products of the dissolved proteins, and as Bennett[2] points out, this titration with methyl orange estimates the total alkalinity. However, by the aid of the ionic theory and the employment of the comparator recently described[3] it has been found possible to determine quickly and with reasonable accuracy, the caustic alkalinity of lime liquors. Consider the case of ammonium hydroxide which is a weak base and therefore is only slightly dissociated into ions in aqueous solution.

$$NH_4OH \rightarrow NH_4^{\cdot} + OH'.$$

By the Law of Mass Action we have :

$$K = \frac{[NH_4^{\cdot}]\,[OH']}{[NH_4OH]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where K is a constant known as the dissociation constant, and at 25° C. has a value of 2.3×10^{-5}. $[NH_4^{\cdot}]$ denotes the concentration of ammonium ions, $[OH^1]$ the concentration of hydroxyl ions and $[NH_4OH]$ is the concentration of the undissociated ammonium hydroxide. As $[NH_4^{\cdot}]$ or $[OH']$ is relatively very

[2] H. G. Bennett, *Collegium* (London), 255-266, 313-322, 329-335, 1915; This Jour., 11, 98 (1916).

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small compared with $[NH_4OH]$ we may regard the latter as constant so that the above equation may be simplified to :

$$[NH_4\cdot] \times [OH'] = \text{constant} \ldots\ldots\ldots\ldots \quad (2)$$

If now a considerable quantity of $NH_4\cdot$ ion be added to a solution of ammonia, as an ammonium salt, *e. g.* ammonium chloride which is almost completely ionized in dilute solution, we have $[NH_4\cdot]$ considerably increased, but as the product $[NH_4\cdot] \times [OH']$ must remain constant it follows that $[OH']$ must be correspondingly decreased.

This reasoning is exactly analogous to that of the case of acetic acid and sodium acetate, discussed in the previous paper[3] except that in this latter case the $[H\cdot]$ is considerably decreased by the addition of sodium acetate to the weak acetic acid. Michaelis[4] has calculated the $[OH']$ of various mixtures of ammonium hydroxide and ammonium chloride, which are given in the following table. At 18° C. however :

$$[H.] \times [OH'] = 0.64 \times 10^{-14}$$

So that, knowing $[OH']$ it is possible to calculate $[H\cdot]$. For curve plotting the symbol P_H which is $-\log_{10}[H\cdot]$ is used, therefore both $[H\cdot]$ and P_H values are appended to Michaelis' figures.

TABLE I.

Calculated Figures by Michaelis Showing $[OH']$ of Various Mixtures of Ammonium Hydroxide and Ammonium Chloride, and also the Corresponding $[H\cdot]$ and P_H Values.

Ratio NH_4OH : NH_4Cl	% N/10 NH_4OH	% N/10 NH_4Cl	$[OH']$	$[H\cdot]$	P_H
32 : 1	96.7	3.3	6.4×10^{-4}	1×10^{-11}	11.0
16 : 1	94.1	5.9	3.2×10^{-4}	2×10^{-11}	10.7
8 : 1	88.9	11.1	1.6×10^{-4}	4×10^{-11}	10.4
4 : 1	80.0	20.0	8×10^{-5}	8×10^{-11}	10.1
2 : 1	66.7	33.3	4×10^{-5}	1.6×10^{-10}	9.8
1 : 1	50.0	50.0	2×10^{-5}	3.2×10^{-10}	9.5
1 : 2	33.3	66.7	1×10^{-5}	6.4×10^{-10}	9.2
1 : 4	20.0	80.0	5×10^{-6}	1.3×10^{-9}	8.9
1 : 8	11.1	88.9	2.5×10^{-6}	2.6×10^{-9}	8.6
1 : 16	5.9	94.1	1.2×10^{-6}	5.2×10^{-9}	8.3
1 : 32	3.3	96.7	6×10^{-7}	1×10^{-8}	8.0

[3] W. R. Atkin and F. C. Thompson, *J. S. L. T. C.*, 143, 1920.
[4] L. Michaelis, *Die Wasserstoffionenkonzentration*, Berlin, 1914.

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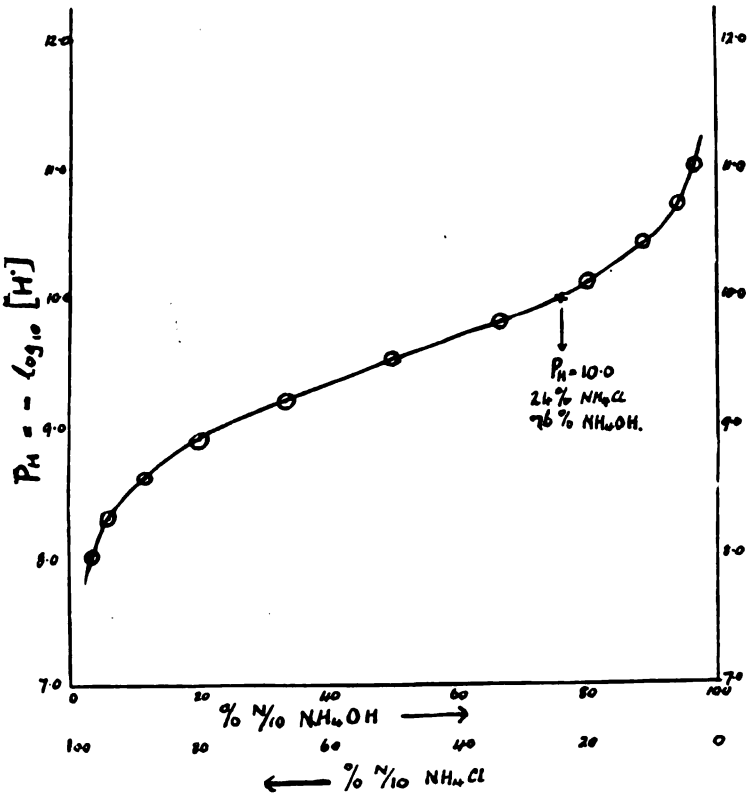

It must be pointed out that dilution has little influence on the (OH′) of mixtures of ammonium hydroxide and ammonium chloride as it is really the ratio $\frac{[NH_4OH]}{[NH_4^+]}$ that is the deciding factor as will be seen by re-writing equation (1) in the form :

$$[OH'] = \frac{K \times [NH_4OH]}{[NH_4^+]} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Thus from the table and curve it follows that a mixture of equal parts of ammonium hydroxide and ammonium chloride has :

$$[OH'] = 2 \times 10^{-5},$$

corresponding to a P_H value of 9.5.

Now consider what happens when a solution of ammonia is titrated with standard acid using phenolphthalein as indicator. Phenolphthalein has a range of color change from $P_H = 8.3$ (colorless) to $P_H = 10.0$ (deep red). Thus at $P_H = 8.3$ am-

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monia is 94 per cent. neutralized, whereas at $P_H = 10.0$ it is only 24 per cent. neutralized.

Not only have we to consider the ammonia, however, but Stiasny's results[5] seem to suggest that the presence of calcium salts might have a profound influence on the [OH'], owing to the formation of complex calcium-ammonia ions but experiments carried out on the following lines proved conclusively that calcium salts do not alter the [OH'] of mixtures of ammonia and ammonium chloride to any appreciable extent.

Various mixtures of N/10 ammonia and N/10 ammonium chloride were made up and the P_H determined exactly as in the manner recently described for the determination of acidity in tan liquors (*loc. cit.*) except that of course a different indicator (phenolphthalein) and different standards were used. These standards were made up according to the instructions given by Cole[6]. The actual values of P_H obtained were found to agree very well with the calculated figures of Michaelis.

The P_H values of various mixtures of ammonia and ammonium chloride to which varying quantities of N/5 calcium chloride or N/10 sodium chloride had been added were determined as shown in the following table:

Mixture consisting of					
cc. N/10 NH_4OH	cc. N/10 NH_4Cl	cc. distilled water	cc. N/10 NaCl	cc. N/5 $CaCl_2$	P_H observed
5	5	10	—	—	9.45
5	5	—	—	10	9.45
5	5	—	10	—	9.45
3.9	6.1	10	—	—	9.3
3.9	6.1	—	—	10	9.3

From these results it will be obvious that calcium salts do not cause any appreciable differences in the P_H and therefore in [OH'], so that on titrating a lime liquor with N/10 HCl. the calcium or sodium chlorides so formed will not affect the [OH'] of the ammonium hydroxide.

The effect of hydrosulphides must now be considered. Sodium sulphide is hydrolytically dissociated in solution as follows:

$$Na_2S + H_2O \rightarrow NaOH + NaSH$$

[5] E. Stiasny, *Der Gerber*, 1906, translated, *J. S. L. T. C.*, 1919; Abs. This Jour., **15**, 172 (1920).

[6] S. W. Cole, *Practical Physiological Chemistry* (published by Heffer, Cambridge).

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The caustic soda of course forms part of the caustic alkalinity but sodium sulphydrate is also hydrolyzed to some extent in aqueous solution.

Walker found experimentally that N/10 NaSH was hydrolyzed to the extent of 0.14 per cent.:

$$NaSH + H_2O \rightarrow NaOH + H_2S$$

whence $[OH^1] = .0014 \times 0.1$

$= .00014$ or 1.4×10^{-4} g. moles per liter.

Knowing the dissociation constant of H_2S, which is a very weak acid, it is possible to calculate the $[OH^1]$ of N/10 NaSH.

We have $NaSH + H_2O = NaOH + H_2S$.

If therefore we have 1 mole of NaSH in "v" liters of water and of this a fraction "x" is hydrolyzed it has been shown[7] that:

$$x = \sqrt{\frac{v \times Kw}{ka}}$$

where Kw is the dissociation constant of water (at 25° C. $Kw = 1.2 \times 10^{-14}$) and ka is the dissociation constant of H_2S ($ka = 5.7 \times 10^{-8}$ at 25° C.), so by substituting these values in the above equation and putting:

$v = 10$ (for decinormal NaSH)

$$\text{we have } x = \sqrt{\frac{10 \times 1.2 \times 10^{-14}}{5.7 \times 10^{-8}}} = 1.45 \times 10^{-3}$$

or the concentration of NaOH and consequently of the OH^1 ion is 1.45×10^{-3} moles in 10 liters,

or $[OH^1]$ is 1.45×10^{-4} Normal—a result that agrees with Walker's experimental figures.

Now in practice lime liquors are seldom used with a higher concentration of sulphide than corresponds to N/20 in sodium sulphydrate.

If we substitute $v = 20$ in the above equation we then have:

$$x = \sqrt{\frac{20 \times 1.2 \times 10^{-14}}{5.7 \times 10^{-8}}} = 2.05 \times 10^{-3}$$

$$\text{or } [OH^1] = 2.05 \times 10^{-3} \times 0.05$$

$$= 1.025 \times 10^{-4} \text{ normal}$$

which at 25° C. corresponds to $[H^1]$ of 1.15×10^{-10}

or P_H value of 9.93, *i.e.*, practically $P_H = 10.0$.

[7] W. C. McLewis, *A System of Physical Chemistry* (Longmans), Vol. I, p. 245.

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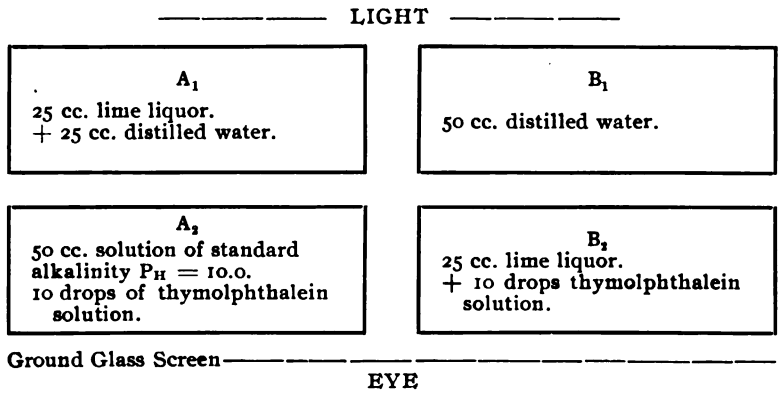
From the above it is clear that if a lime liquor be titrated to a point corresponding to $P_H = 10.0$ the sodium and calcium hydroxides will be practically completely neutralized, the ammonia will be neutralized to the extent of 24 per cent. (see curve) but the sulphdrate will not have been affected. Thus the titration will be a measure of $a + b + 0.24d$. It is worthy of note that in all titrations to $P_H = 10.0$ no smell of escaping H_2S was detected, but if the titrations were carried beyond this point the smell of H_2S became quite distinct.

Hence by estimating the ammonia, preferably by distillation in vacuo as described by Thompson and Suzuki[8] the value of $a + b$ (the caustic alkalinity) may be obtained from two determinations instead of four as described in the previous paper.

The choice of indicator in order to titrate to a P_H value of 10.0 is important. Phenolphthalein has a range of color change from 8.3-10.0, and at the latter value it is colored deep red. As a general rule an indicator is not suitable near the limits of the color change so that the most suitable indicator for our purpose appears to be thymolphthalein which changes from colorless to blue over the range of P_H 9.3 to 10.5. Thus at $P_H = 10.0$ we are near the middle point of the color change.

The titration to a value of $P_H = 10.0$ was carried out in the comparator previously described (*loc. cit.*) using boiling tubes (6 in. × 1 in.) of the same internal diameter, as shown in the diagram:



[8] F. C. Thompson and K. Suzuki, *J. S. L. T. C.*, 140, 1917.

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N/10 HCl was run slowly into tube B_2 stirring continuously and when the match was nearly complete distilled water added until the total volume in B_2 was nearly 50 cc. (It is convenient to scratch a mark on the boiling tubes corresponding to a capacity of 50 cc.) The titration was continued until the color seen through the tubes A_1 and A_2 matched that seen through B_1 and B_2.

It was noted that the blue color of the thymolphthalein indicator faded after some time, so it is better to make up tube A_2 each time that a titration is being carried out.

As the standard solution of $P_H = 10.0$ a mixture of 76 per cent. N/10 NH_4OH and 24 per cent. N/10 NH_4Cl was used. A liter of solution of this composition may be made up and kept in a stoppered bottle, the thymolphthalein being added to 50 cc. as required.

Determinations of the caustic alkalinities of four lime liquors were made and these results compared with results obtained by the method previously described.[9] All titrations are given in terms of cc. N/10 acid or alkali per 25 cc. of filtered lime liquor.

	No. of lime liquor	1	2	3	4
Method described in this paper	Titration to $P_H = 10.0$ ... . $(a + b + 0.24d.)$	10.2	16.45	16.8	17.05
	Ammonia (d).....	0.1	12.1	4.8	7.0
	0.24d.	0.02	2.9	1.15	1.7
	$\therefore a + b$..... (caustic alkalinity)	10.18	13.55	15.65	15.35
Method of Atkin and Palmer[1]	1st H.CHO titration..... $(a + b + c$ — amino acids)	9.1	13.3	19.9	18.9
	2nd H.CHO titration..... $(d +$ amino acids)	1.1	12.6	5.0	7.35
	Ammonia (d).....	0.1	12.1	4.8	7.0
	Sulphide (c).....	0.0	0.6	4.4	3.7
	$\therefore (a + b)$..... (caustic alkalinity)	10.1	13.2	15.7	15.55

It will thus be seen that the agreement between the two methods is quite satisfactory.

SUMMARY.

A quick method for determining the caustic alkalinity of lime liquors involving:

[9] W. R. Atkin and W. E. Palmer, *J. S. L. T. C.*, III, 1920.

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A. A titration with standard acid to a definite value of P_H (= 10.0) using the comparator and thymolphthalein as indicator. This titration is a measure of the caustic alkalinity plus 24 per cent. of the ammonia but does not cause any decomposition of the sulphide present.

B. A determination of the ammonia by distillation.

Then Titration A — 0.24 × Titration B = caustic alkalinity.

BOOK NOTICE.

IRON TANNING; ITS DEVELOPMENT AND PRESENT STATE. By Josef Jettmar. Verlagsbuchhandlung Schulze & Co., Leipzig. Price 20 Marks.

This book which the author dedicates to the American Leather Chemists should be of particular interest to leather chemists in view of the tempting possibilities this subject has always held. Great strides have been made in recent times toward solving the problems of producing a serviceable leather with iron salts and success has already been claimed particularly in combination with chrome salts.

The book consists of a review of all known work on this subject up to the present time and is divided into five sections as follows:—(1) History of Iron Tanning, (2) Patents on Iron Tanning, (3) Iron and Its Compounds, (4) Theory of Iron Tanning, (5) The Execution of Iron Tanning.

ABSTRACTS.

Organic Acids in the Tannery. ANON, *Lea. World,* Sept. 16, 1920. Among the number of purposes to which organic acids are used, is mentioned the following:—(1) Soaking of dried hides or skins, (2) deliming or bating, (3) as a pickling agent before chroming, (4) to increase the acidity of tan liquors, (5) scouring or clearing the grain of fancy leathers, (6) in conjunction with aniline dyes, (7) as a component of finishes and bleaching agents.

Formic acid is most used for soaking of dry hides and skins, lactic and butyric acids for deliming. In pickling stock to be chrome tanned, 10 per cent. of salt and 2 per cent. of formic or 1 per cent. of butyric are used, dissolved in 20 gallons of water per 100 pounds of skin. Formic and acetic acids are used in connection with acid dyes to liberate the color acid and in connection with basic dyes as retarding agents to prevent a too rapid absorption of the dye. Another reason for using acid in the dye liquor is to correct any existing hardness of the water. When dyeing fancy colors on light calf or sheepskins, particularly in vegetable tannages, a clearing with acetic or oxalic acid in weak solution is often given. Vegetable tanned leathers for a natural or russet color receive a partial bleaching before dyeing in a 2 per cent. solution of borax followed by a 2 per cent. solution of lactic acid. A ½ to 1 per cent. solution of oxalic acid is a satisfactory bleach for tanned leather.

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Acetic acid is a common component of finishes or seasonings for glazed leathers, particularly in combination with albumin in a clear or transparent glaze. In the manufacture of box or glacé leather it is fairly common practice to sponge the grain with a solution of lactic acid before applying the season.

The Influence of Potassium Permanganate on Kjeldahl Nitrogen Determinations. By D. C. COCHRANE, *J. I. and E. C.*, **12**, 1195 (1920). The claim that the addition of permanganate in the Kjeldahl method causes loss of nitrogen is not substantiated by the results obtained on feeds and feces. One gram of material, 0.3 gram of metallic mercury and 30 cc. of concentrated sulphuric acid were used for digestion. This was boiled for an hour longer after the solution became clear, removed immediately and sufficient potassium permanganate added in small portions to produce a constant pink or green color. Not more than 10 seconds elapsed between the turning out of the flame and the addition of the permanganate and care was taken to avoid flashing on the addition. About 50 mesh permanganate gives the best results, if it is too fine flashing occurs with a resultant loss of nitrogen.

Nitrogen determinations made, using the same method without the addition of permanganate on feeding stuffs and feces are less concordant, and are uniformly lower than those in which permanganate is used.

Mangrove Tanning. *Science and Industry*, **2**, 437 (1920). A summary of a report furnished to the Institute of Science and Industry, Commonwealth of Australia by the Queensland Tanning Committee on a method for obtaining an improved color in mangrove tanned leather. The material investigated was a mixture of red mangrove (*B. ruginera Rheedi*) and black mangrove (*Rhizophora Mucronata*). The only promising results were obtained by the precipitation from the extract of sufficient aluminum salts to remove about 20 per cent. of the tannins present. Extract of 1.05 sp. gr. requires about 1 pound of aluminum sulphate to 40 gallons and about 1 pound of soda ash, in the form of strong solution to cause precipitation. The precipitate requires about 24 hours to settle properly. Sufficient coloring matter is removed to give a leather which is brown in color and lighter in shade than the untreated material. The acidity of the extract is restored to its normal value by the addition of acid before use. The committee recommends that a series of large scale experiments be carried out before establishing the process on a commercial basis.

Manufacture of Tanning Extract. By C. L. WATSON, *Hide and Lea.*, Oct. 2, 1920, p. 73. An article dealing with the location, construction and practical operation of a chestnut wood extract plant. The author treats in detail of the construction of a plant so as to have its buildings and machinery arranged in a logical and economical manner and gives the plan of such a plant. The operation of a ten leach section and of a multiple effect evaporator is discussed. Three factors of importance in leach-

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ing are:—quantity of water to be used for thorough leaching, time of treatment of wood, and temperature maintained in the various leaches of the set.

Effect of Relative Humidity on Leather Belting. By F. W. Roys, *Hide and Lea.*, Jan. 1, 1921, p. 21. The procedure adopted in this investigation was as follows:—(1) A 4-inch single, oak tanned leather belt about 25 feet long of first quality was selected. (2) The belt was made endless and operated over a pair of 24-inch diameter, 6-inch crown face cast iron pulleys. (3) The belt speed was maintained at about 1,900 feet per minute. (4) The transmitted horse-power was kept constant. (5) The temperature was kept constant except in the last part of the work when the sum of the belt tensions was kept constant instead. The above conditions being fixed it was considered that three important ones were left to vary:—(*a*) The belt length, (*b*) the sum of the tensions in the tight and slack sides of the belt, (*c*) the relative humidity.

Three sets of experiments were made to study the three variables:—(1) Determination of the relation between center distance and the sum of the tensions, relative humidity remaining constant. (2) Determination of the relation between center distance and relative humidity, the sum of the tensions remaining constant. (3) Determination of the relation between relative humidity and the sum of the tensions, center distance remaining constant.

The results show that the effect of a change in relative humidity is greater at higher humidities than at low; that increasing the humidity shows practically immediate results, while a decrease takes a longer time to be effective. Graphs are given, based on the results of the tests, which show that the modulus of elasticity of the belt is different for different values of relative humidity; that the stretch of the belt is greater for a given change in tension at a high humidity than at a low; and that the stretch of the belt is greater for a given change in humidity at high tensions than at low tensions.

Note on the Swelling of Gelatine in Acids. By W. R. Atkin, *J. S. L. T. C.*, 4, 268 (1920.) A description of recent work by J. Loeb on the effects of acid treatment of powdered gelatine on various properties such as swelling, viscosity and osmotic pressure is given, and the concordance of the results with those obtained by Procter and his collaborators is emphasized. It is considered that additional evidence is thus provided as to the soundness of the Procter-Wilson theory of the swelling of gelatine in acids. The actual hydrion concentration is shown to be the factor determining swelling irrespective of the nature of the acid except in the case of sulphuric acid, but other dibasic and tribasic acids behave like monobasic acids, showing a maximum swelling of gelatine when the [H·] in the jelly is 0.0001 Normal ($P_H = 3.0$), and this has been shown previously to be equivalent to a concentration of the external equilibrium acid of [H·] = 0.004 Normal ($P_H = 2.4$).

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Chrome Tanning II. The Determination of the Basicity Figure of One-Bath Chrome Liquors. By D. BURTON and A. M. HEY, *J. S. L. T. C.*, 4, 272 (1920). It is shown that carbon dioxide functions as an acid in a chrome liquor, and that the present method of determining the acid is therefore inadequate since it fails to take account of this and other volatile acids.

In the determination of the basicity figures of one-bath chrome liquors, it is recommended that the acid shall be determined by adding the caustic soda to the diluted liquor in the cold, and that the addition shall be continued during the period of heating up to the boiling point, and then until the pink color persists after one minute boiling.

Electro-Chemistry of Tannins. By GEORG GRASSER, *Coll.*, 597, 17; 598, 49; 600, 137; 601, 200 (1920). For the preliminary work a 3-cell apparatus was used. This consisted of a beaker containing the material to be tested, and in which were suspended two tubes each covered with parchment paper at the bottom and containing distilled water and an electrode. After the current had been allowed to act from 60 to 480 minutes the solutions in the tubes were tested with various reagents such as solutions of gelatine, iron salts, $BaCl_2$, etc., in order to determine the pole to which the material moved. Tannin under a PD of 80 volts and gelatine under a PD of 200-140 volts moved towards the cathode. Neradol D under a PD of 40-60 volts moved towards both poles, but the movement towards the anode predominated at the end. In the remainder of the work a 2-cell apparatus was used consisting of a beaker containing both water and a gauze electrode. In the beaker was suspended a tube covered with parchment at the bottom and which contained the other electrode and the solution to be tested. Pyrocatechol moved toward the cathode and this movement was increased by adding either formic acid or NaOH to the pyrocatechol solution. This solution, after the electro-osmosis, was entirely precipitated by gelatine, but was not capable of tanning skins. Resorcin and phloroglucin each moved toward the cathode while the movement with hydroquinone was indistinct. Gallic and pyrogallic acids alone did not move with the current, but each moved toward the cathode when formic acid was added. The electro-dialysed pyrogallic acid solution and the anode solution from the electro-dialysis of resorcin gave precipitates with gelatine, but had no tanning action. Tannin showed a movement toward the cathode in that the cathode solution gave a blue color with iron salts while the anode solution gave a steel green color. This blue color, however, developed only in a slightly alkaline solution and changed to green if the solution was acidified with acetic acid. No definite movement was found if NaOH or HCl were added to the tannin solution while acetic acid and also sodium acetate caused a movement of the tannin to both poles. It was not possible to get a movement of tannin to the cathode without the formation of secondary insoluble products. Algarobilla changed rapidly to a product which changed iron salts green instead of blue and which did not precipitate gelatine. The movement of this

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material was toward the anode since a precipitate with gelatine was obtained only with the anode solution. Divi-divi alone showed no movement, but moved toward the anode when formic acid was added. In the latter case a substance was formed at the cathode which colored iron salts deep blue, but which did not precipitate gelatine. This same substance can be produced by hydrolyzing a divi-divi solution with NaOH.

Oak bark tannin was rapidly decomposed during electro-dialysis and only a small amount of a material, which colored iron salts brown, reached the anode. From oakwood tannin solution a gelatine precipitating substance moved to the anode while at the cathode a substance was found which colored iron salts deep green. If acetic acid was added to the solution before the electro-dialysis the cathode solution gave the oakwood reactions with sodium sulphite, calcium hydroxide, etc., but colored iron salts blue, while the anode solution colored iron salts deep green, but failed to give the other reactions. This tannin must therefore consist either of two differently charged tannins or it is broken up by the current into two different substances which precipitate gelatine. Pine bark tannin moved to the anode, but suffered considerable decomposition. The electro-dialysis of galls was very similar to that of tannin except that the anode solution gave a brown color with iron salts similar to the color given by the non-tans at the cathode. With catechu and gambier, substances were found at both electrodes which precipitated gelatine and gave a dark color with iron salts, but gave none of the characteristic reactions for these tannins. An insoluble green mass separated from the catechu solution during the purification by electro-dialysis, but dissolved at once in sodium hydroxide, giving a clear red solution similar to the original. Catechu must therefore consist principally of a sodium salt. Mangrove also precipitates as the current passes, but re-dissolves readily in sodium hydroxide, showing that it is also a sodium salt. The fact that these two tannins are sodium salts is closely related to their ready solubility in water and their poor tanning action. The tannins from chestnut wood, mimosa, sumach, and myrobalans moved to the anode, but no special characteristics were noted. The electro-dialysis of maletto was characterized by a cherry red dye which moved to the cathode, while the tannin moved to the anode. Quebracho was a very poor conductor and little tannin was found at the electrodes. Also there was very little decomposition of the tannin by the current. However, when acetic acid was added there was a distinct movement to the cathode. From valonia the tannin moved to the anode, while a substance moved to the cathode which gave the usual reactions with iron salts and potassium nitrite, but did not precipitate gelatine. The tanning principle of sulphite cellulose, lignin sulphonic acid, moved to the anode as would be expected. The tanning principle of Neradol D moved only to the anode, and this anode solution colored iron salts greenish black, showing that the usual blue color of Neradol with iron salts is due to impurities.

The electro-dialysis of several mixtures of quebracho with other tanning materials was also carried out. If quebracho extract had been

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adulterated with mangrove the cathode solution was blood red within 15 minutes. With pure quebracho this solution was brown and with sulphited quebracho it was colorless. The presence of electrolytes, especially sodium salts, made the test more delicate. Chestnut could be detected in quebracho extract by the fact that the anode solution was colored deep blue with iron salts and gave a fuchsin color with concentrated sulphuric acid. If sulphite cellulose, Neradol D, sodium sulphite or bisulphite were present in quebracho extract the voltage during electro-dialysis was very low and sulphates or sulpho-salts moved to the anode where they could be tested for with barium chloride. When concentrated sulphuric acid was added to the anode solution, it was colored brown if Neradol was present and a fuchsin color, if the sulphites were present. If dextrose was present in quebracho extract, even if only in small amount, it could be detected by testing the solutions at the poles with potassium hydroxide and *o*-nitrophenylpropionic acid (see *Coll.*, 1910, p. 301, and 1919, p. 309). The electro-dialysis of quebracho mixed with either auramine or methylene blue did not lead to results of value. An electro-dialysis was made of the calcium, lead and iron compounds of quebracho extract formed by precipitating the extract with salts of these metals and dissolving the washed precipitate in dilute acetic acid. A small amount of tannin moved to the anode from the lead compound, but practically none from the other compounds. There was no movement of the tannin in a mixture of quebracho and strychnine, but the strychnine moved quantitatively to the cathode, indicating that this method may be of use in the separation of alkaloids. Albumin, when present in quebracho extract, moved to the cathode, but the tannin did not move at all in concentrated solution and only in very small amount in a dilute solution (a spent tan liquor). The electro-dialysis of quebracho solutions which had been hydrolyzed by boiling with either sodium hydroxide or sulphuric acid did not cause the separation of substances having any of the characteristics of the hydrolyzed material. The movement was very slow and insoluble substances began to form before the movement had progressed far. Neither was this method suitable for the isolation and investigation of the decomposition products formed by oxidizing quebracho with nitric acid or bromine for the current caused a further decomposition. I. D. C.

Application of the Acetylated Phenol Carboxylic Acids in the Synthesis of Depsides. By E. FISCHER and A. R. KADISADE, *Ber. d. d. chem. Ges.*, 1919, *72*; abst. in *Coll.*, 605, 442, 1920. In the preparation of simple depsides the carbomethoxy compounds of the phenol carboxylic acids can be replaced by the acetyl compounds as in the synthesis of digallic acid. With *p*-oxylbenzoic the synthesis proceeds according to the old scheme whereas the acetyl compound would offer the same advantage as in the preparation of digallic acid. R. W. F.

Some Problems of Tanning Chemistry Research. By E. STIASNY, *Coll.*, 602, 255-66, 1920. There is need for a more thorough study of collagen and similar hide complexes. In the literature many collagens are spoken

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of, but the cause of the differences has not been determined. Collagen from different sources such as hide, sinews, bones or fish scales, show differences which are expressed in ease of forming glutin. Similar differences occur with hide colloids of different animals and even with the same kind of animal, but of different age. The generally accepted view of the structure of the collagen molecule that it consists of a chain of amino-acids held together by pure chemical bonds is questioned by some chemists who believe that while the peptones are formed by the linking together of amino acids in the usual way, the peptones are in turn joined together much less firmly in building up the protein molecule. They suggest that the peptones are surrounded by a water film of greater or less thickness and are joined to adjacent peptones by and through these films by a force similar to auxiliary valence. As examples of a similar nature may be cited the well defined crystalline compounds which Pfeiffer and his co-workers obtained with amino acids and metal salts. In further support of the above view the following facts are presented. By the action of pepsin only peptones are formed, while trypsin which attacks the —CO—NH— group, causes a splitting up of the protein into amino acids. Reference is made to the work of Obermeyer and Pick (*Beiträge zur chem. Physiol. u. Pathol.*, 7, 331, 1905) and of Sorensen (*Biochemische Zeitschrift*, VII, 45, 1908). The swelling action of acid depends upon an increase in the water film around the peptone micell so that the affinity between the peptones is lowered. This action is increased by pepsin leading finally to an isolation of the peptones by a partial splitting up of the proteins. Trypsin behaves quite differently in that it acts on most proteins directly. It does not attack collagen, however, until it has been swollen by acid probably because the water films are originally very thin and the —CO—NH— groups are very firmly bound. The resistance of different collagens to conversion into glutin depends on their water content and this resistance can be increased by drying with heat or alcohol. The influence of the size of the water film upon the ease of division of a peptizable body and the probability of the union of peptone within the complex in a different manner from that in which the amino acids are held to the peptones and peptides are supported by the work done in other lines of chemistry, among which are mentioned Heinz's work on the relation between the water content of freshly precipitated stannic acid and its solubility in sodium hydroxide; Cohnheim's article on the chemistry of albumins; and K. Hess' on the constitution of cellulose. Not only is this problem of theoretical interest in determining the constitution of hide, but also of practical value since it is believed that when the collagen complex and its components can be clearly recognized as chemical individuals, the problems of hide swelling and the conduct of hides before and during tanning will be readily solved. Concerning the vegetable tannins, Stiasny says that the present qualitative division is too old and is not sufficiently grounded upon decomposition products. Instead of the violent KOH fusion a milder decomposition should be used. While it could not be confirmed, there are indications that the division into the two

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broad classes, catechol and pyrogallol, with formaldehyde might depend upon the degree of methylation which is very common in plants. Resorcin and gallic acid are precipitated by formaldehyde while dimethyl resorcin and trimethyl-gallic acid are not precipitated. But the difference in the relative carbon content of the two groups is not in harmony with the methylation theory. The cause of this difference in carbon is obscure. It might be due to condensation products which form in the plant with the formaldehyde always present. An investigation of the formation of tannin should include a study of the transformation which the tannin of leaves undergoes upon passing into the bark and wood. The structural formulas of Euler (*Grundlagen und Ergebnisse der Pflangenchemie, 2*, p. *222*) showing the formation of tannin in leaves are given. How the tannin molecules are built up according to Euler, what part the formaldehyde and sugars of the plant play, should be studied. Büsgen's researches in which he showed that tannin is formed from sugar by leaves should be repeated on a larger scale to show the relations if any between the kinds of tannin formed and the solutions used. While the constitution of the tannins is of utmost importance, it is possible that in tanning differences in constitution will have less effect than difference in size of particles or in general the colloidal condition. The relation between the rate of diffusion or degree of dispersion and the presence of non-tans or electrolytes as affecting the tanning properties should be investigated as should also the possibilities of selective adsorption. R. W. F.

Contribution to the Knowledge of Collagen. By AUGUST EWALD. Abst. in *Coll.*, 605, 446-7, 1920, from *Z. f. physiol. Chem.*, 105, 115-157, 1919. Connective tissue fibrils from mouse tail and frog leg sinews were subjected to hot water and the contracting temperature and amount of contraction observed. Contraction was gradual at 63°-68° C. and sudden 69°-70° C. It amounted to 74 per cent. of the original length. With pure collagen from trypsin action on mouse tail sinews shrinking commenced at 56°-60° C. and at 65° C. it took place almost instantly. Such treated sinews shrunk so that their final length was only 9.3 per cent. of their original length. These differences between the untreated and treated sinews the author attempts to explain on the assumption that it is only a matter of cellular elements and elastic fibers and not to any change which the collagen itself undergoes upon trypsin treatment. Further studies with differently treated fibrils were undertaken. After treatment with 0.001 per cent. HCl the temperature at which contraction started was lowered to 46°-50° C. At higher temperature (60°-70° C.) the contraction occurred rapidly and attained the same maximum as with untreated fibrils (74 per cent. of the original length). Upon acid treatment in common salt solution followed by washing the fibrils in salt solution and finally in pure water so that any swelling is avoided, the behavior of such fibrils towards shrinking is in nearly complete harmony with that of the untreated ones. Weak alkali (0.02 per cent. NaOH) promotes the shrinking action some. Long treatment with alcohol retards the shrink-

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ing without, however, raising the shrinking temperature, but the final length is less than with the fresh sinews. The alcohol treated fibrils differ from the untreated ones in that despite the greater contraction they have always a somewhat opaque appearance and upon subsequent treatment with cold water there occurs a relengthening of the sinew fiber which is considerably more than with fresh or any other treated fibrils. One-half per cent. osmic acid causes considerable raising of the shrinking temperature (about 15° C.) and the shrinkage is greater than with untreated fibrils. Chromic acid, in the absence of light, has little influence; with light it causes a decided increase in the shrinking temperature. The shrinkage never amounts to more than ⅓ of the original length and the sinews are opaque. Previous treatment with tannin raised the shrinking temperature about 20° C., but the amount of shrinkage remained unchanged. Formaldehyde treated fibrils have a characteristics behavior, gradual shrinking starts at 87° C. and takes place rapidly at 93° C. whereby the contraction amounts to about 66 per cent. of the original length. Upon introducing in cold water the shrunken sinew expands instantly, like a compressed spiral spring, to ⅔ of its normal length. Such sinews contract again at 69° C. to ⅓ of its original length and by long exposure in cold water they come entirely to their original length and form. This behavior may be considered characteristic for collagen. The author considers that this work is in further support of the assertion made by him and Kühne that the recticular connective tissue, as in lymph glands, contains a net of fine collagen fibrils which after trypsin digestion remain and behave exactly as collagen. Formaldehyde treated gelatine showed a similarity to formaldehyde collagen. There remains to mention that the hot water contracted and swollen sinews possess entirely different elasticity than the fresh sinews; they become as elastic as rubber.

R. W. F.

On the Free Amino Groups of Protein. By S. EDLBACHER. Abst. in *Coll.*, 605, 447, 1920, from *Z. f. physiol. chem.*, 107, 52, 1919. According to Kossel and Edlbacher (*Z. f. physiol. chem.*, 107, 45, 1919), dimethyl sulphate in alkaline solution of peptides acts only upon the free amino groups with formation of betaine like bodies, not however upon the imino groups present in peptide compounds. Several proteins were treated with dimethyl sulphate in alkaline solution and the total nitrogen and methyl bound nitrogen determined in the reaction mixture. The "nitrogen methyl number" is defined as the number of methyl groups per 100 atoms of nitrogen which are bound to nitrogen after treatment of the compound with dimethyl sulphate. Gelatine gave a "nitrogen methyl number" of 15.0. By alkali hydrolysis of the gelatine the figure was raised to 89.7. Acid hydrolysis and trypsin digestion increased the methyl figure. A comparison of the "nitrogen methyl number" with that from Sorensen's formol titration and from Van Slyke's method showed no simple relation. Very different proteins show in many cases similar methyl figures, on the other hand there were obtained great differences with closely related

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proteins, as the protamines. The author showed that gelatine yielded neither methoxyl nor methylimid which is in contradiction to Skraup and Boettcher (*M. H.*, 31, 1035, 1910) who found 0.35 per cent. OCH_3 and 1.10 per cent. CH_3 (by nitrogen) and Herzig and Landsteiner (*Bioch. Zeitschi.*, 61, 458, 1914) who found 0.18 per cent. OCH_3 and 1.17 per cent. CH_3 (by nitrogen). R. W. F.

Lignin and Lignin Reactions. By PETER KLASON. Abst. in *Coll.*, 605, 445-6 (1920), from *Ber. d. Chem. Ges.*, 53, 706 (1920). Lignin sulphonic acid, an important constituent of sulphite waste liquor, gives with naphthylamine salts in acid solution, after removal of loosely bound sulphites, a yellow precipitate. Upon warming with dilute alkali this compound goes into solution and a part of the naphthylamine is thrown down which upon extraction with ether gives a clear reddish brown solution. Upon acidifying with hydrochloric acid a similar yellow precipitate is obtained. This behavior indicates the presence of an inner ammonium salt and not a simple naphthylamine salt of lignin sulphonic acid. The author proposes that by sulphite treatment the complex $R-CH=CH-CHO$ in lignin is changed to $R-CH_2-CH(SO_2.OH)-CHO$ which with naphthylamine first forms a simple salt $R-CH_2-CH(SO_2.O.NH_3C_{10}H_7)CHO$. This upon rearrangement of an inner ammonium salt passes over to

The author also comes to the conclusion that coniferyl aldehyde

and coniferyl alcohol are the essential and together the only apparently chemically active constituents at least of the conferous lignins.

R. W. F.

PATENTS.

Synthetic Tanning Agents. British Patent 148,268. M. MELAMID, Freiburg, Breslau, Germany. Feb. 23, 1920. Synthetic tanning agents are prepared by sulphonating the alkali-soluble fractions of anthracene oil or soft pitch, and condensing the sulphonic acids with aromatic sulphochlorides in alkaline solution. According to an example, the parent substance is sulphonated with sulphuric acid monohydrate, the product dissolved in water and neutralized with caustic soda, sodium sulphate is removed by evaporation, and the concentrated solution is mixed with caustic soda and treated with toluene sulphochloride in benzene solution.

Leather. British Patent 148,454. J. J. STOECKLY, Berlin. July 10, 1920. Enamelled or patent leather is hardened during the drying process, either under the action of heat or of ultra-violet rays, or of a combination

of these processes, by submitting the varnished surface to the action of alcohols in liquid or vaporized state. Ethyl, methyl, propyl, butyl, amyl, or other alcohols may be used. A better result is obtained by causing alkalies, such as potassium, sodium, or ammonium hydroxides dissolved in alcohol or other suitable medium, to act on the patent leather. The drying process is stated to be accelerated by these means.

Tanning, Etc. British Patent 148,615. J. MOREL, Grenoble, Isère, France. April 22, 1919. Basic sulphate of chrome ($Cr_2(SO_4)_2(OH)_2$) for tanning, dyeing, printing, dressings, etc., is produced by bringing sulphur dioxide in the gaseous state in contact with an alkaline bichromate or a neutral chromate without addition of sulphuric acid or other reagent. The sulphur dioxide is formed by the combustion of sulphur or of pyrites, and the bichromate or chromate is in solution or in contact with water.

Synthetic Tanning Agents. British Patent 148,738. M. MELAMID, Freiburg, Germany. Feb. 25, 1920. The alkali-soluble fractions of anthracene oil or soft pitch are sulphonated by means of sulphuric acid monohydrate; the products constitute tanning agents.

Synthetic Tanning Agents. British Patent 148,897. CHEMISCHE FABRIKEN WORMS AKT-GES., Frankfurt-on-Main, Germany. July 10, 1920. Synthetic tanning agents are prepared (1) by coupling aromatic compounds containing acid groups with vegetable tanning agents, (2) by coupling water-soluble aliphatic compounds with vegetable tanning agents. According to examples:—A mixture of phenol sulphonic acid and tannin is heated with formaldehyde solution; a mixture of barium cresol sulphonate and tannin is heated with formaldehyde solution and the product acidified; a mixture of naphthalene sulphonic acid and tannin is heated with formaldehyde solution; a mixture of naphthalene and phenol is heated with sulphuric acid, the product is condensed with formaldehyde, and the resulting tanning agent further heated with tannin and formaldehyde solution; coal-tar phenols of boiling-point 185°-200° C. are heated with sodium sulphite and formaldehyde solution, then quebracho extract and formaldehyde solution are added and the mixture further heated; a mixture of glucose and tannin is heated with formaldehyde solution. The products may be used in tanning alone or mixed with other tanning agents or in combined tanning processes using both vegetable and mineral tanning agents.

Synthetic Tanning Agents. British Patent 148,750. GERB-UND FARBSTOFFWERKE H. RENNER & Co., AKT.-GES., Hamburg, Germany (assignees of H. Renner and W. Moeller). June 26, 1920. *Sulphonic Acids.*—Synthetic tanning agents are prepared from coumarone resin by the following processes:—(1) A mixture of coumarone resin with a mono- or polyhydric phenol is sulphonated, with or without the addition of formaldehyde, or a sulphonated coumarone resin is condensed with a mono- or

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poly-hydric phenol, with or without the addition of formaldehyde; (2) a sulphonated coumarone resin is condensed with the resins obtained by alkaline condensation of phenols with formaldehyde, or a non-sulphonated coumarone resin is condensed with the sulphonated phenol-formaldehyde resins; (3) the coumarone resins or their sulphonic acids are condensed with aromatic or "heterocyclic" hydrocarbons, or their sulphonic acids, or with the acid resins from mineral or tar oil purification, or with the products described in Specification 146,166; (4) coumarone resins which contain also indene are condensed and sulphonated by means of sulphuric acid, with or without formaldehyde; (5) the sulphonated or non-sulphonated product of (4) is further condensed and sulphonated, together with phenols, with or without formaldehyde, or with the products of (1), (2) or (3); (6) the products of the foregoing processes are convertetd into quinone-like compounds by oxidation, *e. g.*, by means of ozone, hydrogen peroxide, potassium bichromate or permanganate, or persulphates. According to examples:—A mixture of coumarone resin and phenol is heated with formaldehyde and sulphuric acid; a mixture of coumarone resin and the condensation product from α- or β-naphthol and formaldehyde is heated with sulphuric acid; a sulphonated coumarone resin is heated with the product from anthracene oil described in Specification 146,166, formaldehyde, and sulphuric acid; coumarone resin containing much indene is heated with formaldehyde and sulphuric acid, the product is further condensed with cresol, and again sulphonated; the product of the first example is treated with potassium bichromate. Excess sulphuric acid is removed from the products by means of alkali or barium or calcium hydroxide or carbonate.

Leather. British Patent 149,334. J. J. STOECKLY, Berlin. July 19, 1920. Ultra-violet light obtained by means of a high-frequency spark is used instead of the mercury-vapor lamp for hardening the surface of patent leather. The usual copper or brass electrodes may be used, or aluminum electrodes are stated to be suitable if the energy and frequency of the discharges do not exceed 1 kilowatt or 60 per second respectively. The energy and frequency of the discharges are regulated according to requirements.

Stretching and Scouring Leather. British Patent 150,022. H. KAY, Warrington, Lancashire. May 6, 1919. A machine for stretching and scouring hides, skins and leather.

Leather-Working Machines. British Patent 150,696. TURNER TANNING MACHINERY CO., Peabody, Mass., U. S. A. Aug. 30, 1920. Relates to machines for unhairing, setting-out, putting-out, and like operations.

Leather-Working Machines. British Patent 151,131. T. HALEY & Co. and F. C. HOEFLING, both in Bramley, near Leeds. July 18, 1919. A machine for shaving or similarly treating leather, skins, hides or the like.

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The American Leather Chemists Association

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JOHN HANNA YOCUM,
1870-1921.

WHEREAS, John H. Yocum, a charter member of our Association, one of its early Presidents, one who contributed largely to its advancement and success, an original and brilliant mind, a most kindly and gracious personality, has passed away;

Be it Resolved, That there be inscribed on our records and published in our JOURNAL, this expression of our sense of the great loss we have sustained, and of our sorrow at the passing of one of the foremost American leather chemists.

THE COUNCIL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION.

February 4, 1921.

With the passing of John H. Yocum, the realm of science lost a master mind. His life was devoted to the development and practical application of scientific principles for the advancement of the leather industry. A pioneer—in the early nineties—alone and without precedents, he laid the foundation for the scientific structure that has risen—ofttimes amid prejudice and opposition—to become the accepted medium of establishment of commercial values in the leather industry of this country and a most helpful aid to all engaged in the production of leather. The educated senses of touch and taste—the inherent knowledge of the early tanner—were supplanted through the persistent laborious and personal efforts of John Yocum, by chemical analyses, which through his early practical interpretations, blazed the trail for the high degree of advancement since attained by this industry. No one appreciated better than he, the needs of the tanner for a clearer and better understanding of the hidden reactions that were operating largely uncontrolled in the long time production of leather. In a small laboratory, near New York City, his inventive and original mind, nurtured by years of practical knowledge of the information wanted, worked out by slow stages, the method of tanning analysis that has stood the test of critical periods and prejudiced interests, and remains to-day, with but few minor changes, as he announced it to the scientific world in 1893.

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John Hanna Yocum was born at Ashland, Pa., May 9, 1870, and at the time of his death had rounded out a full half century of usefulness and service. He attended Pennsylvania State College in 1888-1889, but left before the completion of his collegiate career and associated himself with the firm of Horton-Yocum & Company, sole leather tanners, Johnson City, Tenn. With the formation of the United States Leather Company in 1893, he filled the created position of chief chemist, which position he continuously held until 1900, at which time the Yocum Manufacturing Company of Newark, New Jersey, was incorporated and the Yocum-Eachus Laboratory established. From 1901 to 1903 he was general manager of T. P. Howell & Company, leather manufacturers of Newark, New Jersey, from which position he resigned and in 1904, became general manager of J. H. Ladew Company, Newark, New Jersey, sole leather and belting tanners, remaining in this capacity until 1912. The Yocum-Eachus Laboratory was succeeded in 1912 by the Yocum Laboratory and for the next five years, Mr. Yocum devoted himself largely to research work and it was during this period that he was called upon by the Government to act as an expert and in this capacity devised a formula for the prevention and spread of the hoof-and-mouth disease prevalent in hides. On January 1, 1920, the Yocum Laboratories were incorporated, of which he was president until the time of his death. This Company has just completed a large and modern plant at Irvington, New Jersey, for the production of synthetic tanning extracts. He was also president of Yocum-Faust, Ltd., London, Canada, and was a member of the Clarendon, Yocum Co., and The Leth-r-fude Laboratories, Inc.

In addition to the business enterprises above enumerated, Mr. Yocum was one of the founders of the American Leather Chemists Association and served as its president at an early period of its history. Prior to the formation of the American Leather Chemists Association and continuously since 1893, he was affiliated with the Leather Chemists Division of the Association of Official Agricultural Chemists. Also a member of the American Chemical Society, Society of Chemical Industry, and the New Jersey Chemical Society; a member of the Essex County Country Club, West Orange, New Jersey, Chemists Club, New York, Newark Athletic Club, Newark, New Jersey. He was a 32nd

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degree Mason, Knight Templar, and a Noble of Salaan Temple, Newark, New Jersey. He was also a member of the Greek Letter Fraternity Phi Gamma Delta, State College, Penna.

In recognition of Mr. Yocum's many contributions to the scientific world, Pennsylvania State College, in June, 1914, conferred upon him the degrees of B. S. and M. S.

After a life service, principally for the good of others, he contracted a cold while assisting in extinguishing a fire at a tannery whence he had gone in performance of his duties. The cold rapidly developed into pneumonia which caused his death on January 27, 1921.

Thus passed from our midst, one whom we all respected for his brilliant intellect, generous and unselfish personality, loyal and true friendship. For years to come, the name of John Yocum will always be most closely associated with the industry to which he devoted his life's work. Like few scientists, he saw before his death, the idealism of his younger days justified and fulfilled. Peace be to his ashes.

E. J. HALEY.

PROPOSED CHANGES IN THE BY-LAWS.

Section 7(b) to be changed to read as follows:

Mutual Members:

By special arrangement with the Society of Leather Trades Chemists, terminable at will at the end of any calendar year by either party to the arrangement, any member of either Association, upon three months notice, may upon payment of a special fee as set forth in Article 9-B, enjoy at any meeting of the affiliated Association the full priviliges of the class of membership (active or associate) to which he belongs, and receive the JOURNAL of the affiliated Association. Members of the American Leather Chemists Association availing themselves of this privilege are designated mutual members.

Section 9(a) to be changed to read as follows:

Each class "A" member of the American Leather Chemists Association shall pay an annual fee of $10.00, due January 1st, of each year, and there shall be no entrance fee. In addition to the privileges of the Association, payment of the fee shall entitle the member to the JOURNAL of the Association.

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Section 9(b):

Each class "B" member of the American Leather Chemists Association shall pay an annual fee of $12.50, $10.00 of which shall go to the A. L. C. A., and $2.50 to the Society of Leather Trades Chemists.

Each class "B" member of the S. L. T. C. shall pay a membership fee of $12.50, $5.00 of which shall go to the S. L. T. C., and $7.50 of which shall go to the A. L. C. A.

In addition to the rights and privileges described and limited in Section 7(a) and (b), payment of the above annual fee shall entitle the mutual member to receive the Journals of each of the two affiliated Associations.

Section 11:

No person shall be entitled to the privileges of membership whose dues are unpaid. If his dues be unpaid three months after the date when due, no subsequent issued of the JOURNAL shall be sent to the delinquent member until his dues are paid.

If his dues be unpaid eight months after the date when due, the secretary shall notify the delinquent member at that time, that unless payment be made within four months from the date of notice, his name may be struck from the register. At the expiration of the four months, should the dues still be unpaid, the Council may order the name of the delinquent member removed from the register, whereupon he shall cease to have any right, privilege or interest in the Association.

(Signed) H. C. REED, *Secretary.*

COUNCIL MEETING HELD AT NEW YORK CITY, FEBRUARY 4, 1921.

Members present—F. H. Small, H. C. Reed, R. H. Wisdom, J. S. Rogers, C. C. Smoot, III, G. W. Schultz.

The resignation of John Arthur Wilson as vice-president of the Association was presented and accepted.

The resignation of C. C. Smoot, III, as ordinary member of the Council was presented and accepted. C. C. Smoot, III, was elected vice-president to complete the unexpired term of John Arthur Wilson.

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Dr. Thomas Blackadder was elected to fill out the unexpired term of C. C. Smoot, III, as ordinary member of the Council.

A report of the financial condition of the Association was submitted by the treasurer. It indicated that we may safely count on a considerably increased income from membership dues which together with that from the increased amount of advertising in the JOURNAL will enable us to somewhat more than meet our estimated expenses for the current year.

Nominations were made of candidates for the two ordinary members of the Council to be chosen at the coming annual meeting.

Sugar in Tanning Extracts.—It was brought to the attention of the Council that the Association has no method for the determination of sugar in tannin extracts. It was thought desirable that such a method should be incorporated in the methods of the Association, and J. S. Rogers was requested to draw up a method in connection with the work of his Committee on the determination of sugar in leather. If this does not prove possible, the subject should be studied by a Committee next year.

The following matters of business were voted on and disposed of as given below:

Foreign Exchange.—That money accruing to the Society of Leather Trades Chemists and to the American Leather Chemists Association, because of mutual memberships, be balanced so far as possible and the ultimate final adjustment be made on a pound, shilling, and pence basis.

That the fiscal year of the Association be made to coincide with the calendar year, and that a statement of the financial condition of the Association be published in the JOURNAL as soon as possible after January 1st of each year, together with an estimate of the probable expenditures for the year.

By-Laws and Methods.—For purposes of economy it was voted that no booklet containing the By-Laws and Methods be published this year, but that the methods be published in the JOURNAL at the earliest possible date, and members desiring reprints be supplied with the same.

Members in Arrears.—That Journals will not be sent to members whose dues are three months in arrears, and that a proposal

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to change Section II of the By-Laws to cover this point be submitted to the members.

Non-Receipt of Journal.—That claims for Journals not received must be made within 90 days from the date of issue in order to secure replacements without charge. Copies not asked for within this time limit will be charged for at the regular rate.

That the editor, secretary and president be constituted a committee to handle the business questions connected with the publication of the JOURNAL, with power to add to their committee should they desire.

That the president and secretary constitute a committee to arrange the time and place and program of the annual meeting with full power to add to their committee as they may see fit.

AMERICAN LEATHER RESEARCH LABORATORY.

IN CHARGE OF GEORGE D. McLAUGHLIN, University of Cincinnati.

The American Leather Research Laboratory, which had been maintained at New York under the auspices of the Tanners' Council for the past three years, was recently removed to the University of Cincinnati and placed in charge of Mr. George D. McLaughlin. Under an arrangement with the University of Cincinnati, the Laboratory will become a part of the College of Engineering and Commerce and will be known as "Department of Leather Research, Tanners' Council of the United States of America Foundation."

It will be remembered that the Laboratory was organized in 1917 by Dr. J. B. Churchill, who served in the capacity of Director for two years, and it was later in charge of Mr. George L. Terrasse who resigned in the summer of 1920.

In connection with the selection of the University of Cincinnati as the location of the Research Laboratory, it is believed that a few facts concerning the institution will be of interest. The University was founded in 1870 and is one of the few large institutions of learning of a purely municipal nature, as its principal support comes from direct taxation of its citizens. A large portion of the buildings and equipment is new and the entire Univer-

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sity is modern in every respect. The various colleges have a total enrollment of 3,500 students.

Probably the most interesting feature of the University's work is the so-called "cooperative system of technical education," originated by Dr. Herman Schneider, Dean of the College of Engineering. The student, during a portion of his five-year course, alternates each month or half month between study in the University and actual work in a factory. The fact that 6,000 applications have been made for admission to the Engineering College shows conclusively the success of the system. Furthermore, other institutions of the country are adopting it. Inasmuch as there will probably be from year to year a few students in the college who are specially interested in tanning it is expected that some of these will be drawn into the Leather Research Laboratory and later into the tanning industry.

The College of Engineering has on its staff some of the most brilliant scholars and teachers in the world and consequently it is well equipped for carrying to completion the extensive scientific and practical work which it has laid out. Among these are Dr. A. P. Matthews who is probably the leading American biochemist, Dr. Martin H. Fischer, who has an international reputation for his researches in colloid chemistry and its special application to the tissues of the human body, and Dr. William B. Wherry, who is widely known for his bacteriological researches conducted in this country and the Orient.

In appreciation of the choice of the Tanners' Council the University Board of Trustees has voted to create a definite department as stated above.

Mr. McLaughlin, who is in charge of the Laboratory is well known to leather chemists. He began his career in the laboratory of Leas & McVitty and later had charge of the chemical work of Kullman, Salz & Company, of San Francisco. In 1919 he associated himself with Dr. Martin H. Fischer, of the University of Cincinnati for the purpose of devoting his entire time to research work. Already Mr. McLaughlin has laid out plans for some important initiatory work which will be started by him in the near future.

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METHODS OF THE A. L. C. A., 1921.

OFFICIAL METHOD OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION FOR THE ANALYSIS OF VEGETABLE MATERIALS CONTAINING TANNIN.

I. Raw and Spent Materials.

(1) Caution:

Proper care must be taken to prevent any change in the water content of raw materials during the sampling and preliminary operations. (See "General" under Sampling.)

(2) Preparation of Sample:

The sample must be ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(a) The temperature used for drying samples of spent material for grinding must not exceed 60° C.

(b) Samples of raw material too wet to be ground may be dried before grinding as in (a). In this case a preliminary water determination must be made according to (IV) on the sample as received. If the portion of the sample taken for the water determination is in pieces too large to dry properly, it is permissible to reduce these to smaller size as rapidly and with as little loss of water as possible.

(3) Water Determination:

Ten grams of the ground material shall be dried in the manner and for the period specified for evaporation and drying in extract analysis (see IV).

(4) Amount of Sample to be Extracted:

Such an amount of raw material shall be extracted as will give a solution containing as nearly as practicable 0.4 gram tannin to 100 cc. (not less than 0.375 or more than 0.425). Of spent materials such an amount shall be taken as will give a solution of as nearly as practicable the above concentration.

(5) Extraction:

Extraction shall be conducted in an apparatus consisting of a vessel in which water may be boiled and a container for the material to be extracted. The container shall be provided above with a condensation chamber so arranged that the water formed from the condensed steam will drip on the material to be extracted, and

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provided below with an arrangement of outlets such that the percolate may either be removed from the apparatus or be delivered to the boiling vessel. The boiling vessel must be so connected that it will deliver steam to the condensation chamber and that it may receive the percolate from the container. The condensation water from the condenser must be at approximately the boiling temperature when it comes in contact with the material to be extracted.

The material of which the boiling flask is composed must be inert to the extractive solution. Suitable provisions must be made for preventing any of the solid particles of the material from passing into the percolate.

(A) Woods, Barks and Spent Materials:

Five hundred cc. of the percolate shall be collected outside in approximately 2 hours and the extraction continued with 500 cc. for 14 hours longer by the process of continuous extraction with reflux condenser. The applied heat shall be such as to give condensation approximately 500 cc. in 1½ hours.

(B) Materials Other than Woods, Bark and Spent:

Digest the material in the extractor for 1 hour with water at room temperature and then extract by collecting 2 liters of percolate outside in approximately 7 hours.

(6) Analysis:

The percolate shall be heated at 80° C., cooled, made to the mark and analyzed according to the official method of extracts.

II. Analysis of Extract.

(7) Amount and Dilution for Analysis:

(A) Fluid Extracts:

Fluid extracts shall be allowed to come to room temperature, be thoroughly mixed, and such quantity weighed for analysis as will give a solution containing as nearly as possible 0.4 gram tannin to 100 cc. (not less than 0.375 nor more than 0.425). Precautions must be taken to prevent loss of moisture during weighing. Dissolve the extract by washing it into a liter flask with 900 cc. of distilled water at 85° C.

Cooling:

(a) The solutions prepared as above shall be cooled rapidly to 20° C. with water at a temperature of not less than 19° C., be

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made to the mark with water at 20° C. and the analysis proceeded with at once, or

(b) The solution shall be allowed to stand over night, the temperature of the solution not being permitted to go below 20° C., be brought to 20° C. with water at not less than 19° C., be made to the mark with water at 20° C. and the analysis proceeded with.

(B) Solid and Powdered Extracts:

Such an amount of solid or powdered extract as will give a solution of the strength called for under liquid extracts shall be weighed in a beaker with proper precautions to prevent change of moisture. One hundred cc. of distilled water at 85° C. shall be added to the extract and the mixture placed on the water-bath, heated and stirred until a homogenous solution is obtained. When dissolved, the solution shall immediately be washed into a liter flask with 800 cc. of distilled water at 85° C., be cooled, etc., as under (a) above.

NOTE.—It is permissible to make up 2-liter instead of 1-liter solutions dissolving by washing into flask with 1,800 cc. water at 85° C. in case of fluid extracts and 1,700 cc. water at 85° C. in case of solid or powdered extracts.

(8) Total Solids:

Thoroughly mix the solutions; pipette 100 cc. into tared dish, evaporate and dry as directed under "Evaporation and Drying." (See IV.)

(9) Water:

The water content is shown by the difference between 100 per cent. and the total solids.

(10) Soluble Solids:

S. & S. No. 590, or Munktell's No. 1F, 15 cm. single, pleated, filter paper shall be used for the filtration.

The kaolin used shall answer the following test: 2 grams kaolin digested with 200 cc. of distilled water at 20° C. for 1 hour shall not give more than 1 mg. of soluble solids per 100 cc., and shall be neutral to phenolphthalein. To 1 gram kaolin in a beaker add sufficient solution to fill the paper, stir and pour on paper. Return filtrate to paper when approximately 25 cc. has collected, repeating operation for 1 hour, being careful to transfer all kaolin to the paper. At the end of the hour remove solution from filter paper,

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disturbing the kaolin as little as possible. Bring so much as needed of the original solution to exactly 20° C. as described under (7), refill the paper with this solution and begin to collect the filtrate for evaporating and drying so soon as it comes CLEAR. The paper must be kept full and the temperature of the solution on the filter must not fall below 20° C. nor rise above 25° C. during this part of the filtration. The temperature of the solution used for refilling the paper must be kept uniformly at 20° C. and the funnels and receiving vessels must be kept covered.

Pipette 100 cc. of clear filtrate into tared dish; evaporate and dry as under (8).

(11) Insolubles:

The insoluble content is shown by the difference between the total solids and the soluble solids, and represents the matters insoluble in a solution of the concentration used under the temperature conditions prescribed.

(12) Non-Tannins:

The hide powder used for the non-tannin determination shall be of woolly texture well delimed and shall require between 12 and 13 cc. of N/10 NaOH to neutralize 10 grams of the absolutely dry powder.

(a) Digest the hide powder with 10 times its weight of distilled water till thoroughly soaked. Add 3 per cent. of chrome alum, $(Cr_2SO_4)_3K_2SO_424H_2O$, in 3 per cent. solution calculated on the weight of the air-dry powder. Agitate frequently for several hours and let stand over night. Squeeze and wash by digesting with 4 successive portions of distilled water, each portion equal in amount to 15 times the weight of the air-dry powder taken. Each digestion shall last for 15 minutes, and the hide powder shall be squeezed to approximately 75 per cent. water after each digestion except the last, a press being used if necessary. The wet hide powder used for the analysis shall contain as nearly as possible 73 per cent. of water, not less than 71 per cent. nor more than 74 per cent. Determine the moisture in the wet hide powder by drying approximately 20 grams. (See IV.) To such quantity of the wet hide as represents as closely as practicable 12½ grams (not less than 12,2 nor more than 12.8) of absolutely dry hide add 200 cc. of the original analysis solution and shake

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immediately for 10 minutes in some form of mechanical shaker. Squeeze immediately through linen, add 2 grams of kaolin (answering test described under (9)) to the detannized solution and filter through single folded filter (No. 1F Swedish recommended) of size sufficient to hold the entire filtrate, returning until clear. Pipette 100 cc. of filtrate into tared dish, evaporate and dry as in (8).

The weight of the non-tannin residue must be corrected for the dilution caused by the water contained in the wet hide powder.

Funnels and receiving vessels must be kept covered during filtration. Flasks graduated to deliver 200 cc. are recommended for measuring the analysis solution to be detannized.

(b) Digest the hide powder with the amount of water and add the amount of chrome alum in solution directed under (a).

Agitate in some form of mechanical shaker for 1 hour and proceed immediately with washing and subsequent operations as directed under (a).

NOTE.—In order to limit the amount of dried hide powder used, determine the moisture in the air-dry powder and calculate the quantity equal to 12½ grams of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing as nearly as possible 73 per cent. of water. Weigh the whole amount and divide by the multiple of the 12½ grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

(13) Tannin:

The tannin content is shown by the difference between the soluble solids and the corrected non-tannins, and represents the matters absorbable by hide under the conditions of the prescribed methods.

III. ANALYSIS OF LIQUOR.

(14) Dilution:

Liquors shall be diluted for analysis with water at room temperature so as to give as nearly as possible 0.7 gram solids per 100 cc. of solution. Should a liquor be of such character as not to give a proper solution with water of room temperature it is

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permissible to dilute with water at 80° C. and cool rapidly as described under (7, A, a).

(15) Total Solids:

To be determined as in Extract Analysis.

(16) Soluble Solids:

To be determined as in Extract Analysis.

(17) Insolubles:

Determined as in Extract Analysis.

(18) Non-Tannins:

To be determined by shaking 200 cc. of solution with an amount of wet chromed hide powder, containing as nearly as possible 73 per cent. water, corresponding to an amount of dry hide powder shown in the following table:

Tannin range per 100 cc.	Dry powder per 200 cc.
0.35——0.45 gram	9.0——11.0 grams
0.25——0.35 gram	6.5—— 9.0 grams
0.15——0.25 gram	4.0—— 6.5 grams
0.00——0.15 gram	0.0—— 4.0 grams

Solutions to be shaken for non-tannins as in Extract Analysis and 100 cc. evaporated as in Extract Analysis.

IV. Temperature, Evaporation and Drying, Dishes

(19) Temperature:

The temperature of the several portions of each solution pipetted for evaporating and drying, that is, the total solids, soluble solids and non-tannins must be identical at the time of pipetting.

(20) Evaporation:

All evaporation and drying shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer" at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

(21) Dishes:

The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than 2¾ inches diameter nor more than 3 inches in diameter.

V. Determination of Total Acidity of Liquors.

(22) Reagents:

(a) One per cent. solution of gelatine neutral to hematine. The addition of 25 cc. of 95 per cent. alcohol per liter is recommended

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to prevent frothing. If the gelatine solution is alkaline, neutralize with tenth normal acetic acid and if acid neutralize with tenth normal sodium hydroxide.

(b) Hematine. A solution made by digesting hematine in cold neutral 95 per cent. alcohol in the proportion of ½ gram of the former to 100 cc. of the latter.

(c) Acid washed kaolin free from soluble matters.

(d) Tenth normal sodium hydroxide.

Directions:

To 25 cc. of liquor in a cylinder that can be stoppered, add 50 cc. of gelatine solution, dilute with water to 250 cc., add 15 grams of kaolin and shake vigorously. Allow to settle for at least 15 minutes, remove 30 cc. of the supernatant solution, dilute with 50 cc. of water and titrate with tenth normal soda using hematine solution as the indicator. Each cc. tenth normal soda is equivalent to 0.2 per cent. acid as acetic.

VI. General.

23) When materials containing sulphite-cellulose extract are analyzed, the fact that the material contains sulphite-cellulose extract shall be noted on the report.

(24) The test for the presence of sulphite-cellulose in a liquor or extract shall be as follows: Five cc. of a solution of analytical strength shall be placed in a test tube, 0.5 cc. of aniline added and the whole well shaken; then 2 cc. of strong hydrochloric acid added and the mixture again shaken. If at least as much precipitate remains[1] as is obtained when a comparison solution prepared as below is similarly treated, the material shall be held to contain sulphite-cellulose.

The comparison solution shall consist of sulphite-cellulose in the proportion of one part total solids to 2,000 cc. of solution, and as much tanning material, similar to that being tested, but known to be free from sulphite-cellulose, as will make up the solution to analytical strength.

(25) On public analytical work by members of this Association the fact that the Official Method has been used, shall be so stated.

[1] Neradol D gives the same reaction.

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Official Method for Sampling Tanning Materials.

General:

Extract whether liquid or solid, and tanning materials in general all contain moisture. The amount of moisture varies with climatic conditions, but especially in liquid, and in most solid extracts becomes less as the extract is exposed to the air. As the value of any material shown by analysis is directly dependent upon the amount of moisture contained, and as an exposure of a comparatively few moments may alter appreciably the amount of moisture it is apparent that the sampling in all its details should be done as quickly as consistent with thoroughness and with great care to expose the material as little as possible to the air. The portions taken as samples should be placed at once in containers as nearly air tight as possible, and preferably of glass. Wood, cardboard, poorly glazed crockery, etc., are all porous and more or less absorbent and not suitable for retaining samples.

Liquid extract cannot be accurately sampled when it contains any frozen material. A sample of extract taken after live steam has been run into the extract has not the same concentration as the original extract. A sample of spent bark which has been standing where dust from fresh ground bark has sifted into it does not represent the degree of extraction of the spent bark. Samples of liquor which have been kept with no preservative in them for some time do not represent the condition of the liquor when sampled.

All extracts and crude tanning materials shall be sampled as nearly as possible at time of weighing, and for every 50,000 pounds, or less, sampled a sample shall be drawn.

(1) Solid, Powdered and Pasty Extracts:

The number of packages to be sampled out of a given lot shall be ascertained by taking a percentage of the total number of packages in the lot obtained in the following manner: Divide the total number of packages by 100, multiply by 0.02 and subtract from 4.

Thus

$$4{,}700 \div 100 = 47$$
$$47 \times 0.02 = 0.94$$
$$4 - 0.94 = 3.06 \text{ per cent.}$$
$$4{,}700 \times 0.0306 = 144 \text{ packages.}$$

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Provided that for lots of 200 packages and under 5 per cent. of the number of packages shall be sampled, and for lots of 10,000 packages and over 2 per cent. of the number of packages shall be sampled.

Whenever possible very Nth package shall be set aside for sampling while the extract is being moved. When this is not possible, the packages shall be selected from as uniformly distributed parts of the bulk as possible.

Samples of as nearly equal size as practicable shall be taken from each package and these samples shall represent as nearly as may be, proportionally the outer and inner portions of the extract. These sub-samples shall be placed in a clean, dry closed container. When sampling is completed, the whole composite sample shall be broken up until it will pass through a sieve of 1-inch mesh; it shall be reduced to the required bulk by successive mixings and quarterings. From this bulk duplicate samples of at least 6 ounces shall be drawn from opposite quarters by means of a small flat scoop (and not by selecting a handful here and there). The sample shall be enclosed in the smallest clean, dry, glass receptacle, sealed and properly labeled.

NOTE.—Whenever possible the sample should be wrapped in paraffine paper and placed in the smallest straight-side glass receptacle; especially is this desirable during the warmer months of the year.

Sampling at place of manufacture shall be conducted by running a portion from the middle of each strike into a mold holding at least 2 pounds. These sub-samples shall be preserved with proper precautions against evaporation, and be sampled for analysis as above.

(2) Liquid Extracts in Barrels:

The number of barrels of extracts to be sampled out of any given lot shall be not less than 10 per cent. of the whole number of barrels for every 50,000 pounds or fraction thereof. The barrels to be sampled shall be rolled and shaken from end to end until the contents are homogeneous. Whenever this is not possible the heads of the barrels shall be removed and the contents stirred until homogeneous, a sample of equal size to be taken from each barrel. These sub-samples shall be put together in a

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suitable closed container and be thoroughly mixed. From this bulk duplicate samples of at least 4 ounces shall be drawn and preserved in clean, dry, glass containers; sealed and labeled with such distinguishing marks as may be necessary.

(3) Liquid Extract in Bulk:

The extract shall be agitated with air, be plunged or be mixed by some other efficient means until homogeneous. Equal samples shall then be taken from different parts of the bulk, be placed in a proper container, be thoroughly mixed and sampled as described in (2).

(4) Liquid Extract in Tank Cars:

The following methods are permissible:

(a) The extract shall be unloaded into clean, dry containers and sampled according to (3); or,

(b) The extract shall be mixed until homogeneous, by plunging through the dome or other effective means, then numerous equal samples shall be taken from as widely scattered parts of the bulk as possible. These samples shall then be placed in a suitable container, be mixed and sampled as in (2).

NOTE.—As it is almost impossible to secure a homogeneous mixture of the extract in a tank car, this method should be used only when no other is possible. Or,

(c) The extract shall be sampled as follows while the car is being unloaded.—A quart sample shall be taken from the discharge three minutes after the extract has begun to run; another quart sample shall be taken three minutes before the extract has all run out, and three other quart samples shall be taken at equal intervals between these two. These five samples shall be transferred to a suitable container as soon as taken, be thoroughly mixed and sampled as in (2).

(5) Crude Tanning Materials:

A. Shipments in bags, mats or other similar packages.

A number of packages shall be sampled representing 2 per cent. of the weight for every shipment of 50,000 pounds or fraction thereof, by taking representative portions from each package. These sub-samples shall be mixed together and the bulk be reduced by mixing and quartering to the desired size. Duplicate samples

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of not less than 5 pounds each shall be preserved in air-tight containers properly labeled.

B. Shipments in bulk, bark, wood, etc., in sticks.

Sticks shall be taken from at least ten uniformly distributed parts of the bulk, be sawed completely through and the sawdust thoroughly mixed and sampled as in "A."

C. Materials prepared for leaching.

Samples of equal size shall be taken at uniform intervals as the material enters the leach and be kept in a suitable container till sampling is completed. This bulk shall then be thoroughly mixed, be reduced by mixing and quartering, and duplicate samples for analyses of at least 2 pounds in size be preserved in air-tight containers, as in "A."

(6) Spent Materials From Leaches:

Samples of spent material shall be taken from the top, middle and bottom, and in each case from the center and outer portions of the leach. These sub-samples shall be thoroughly mixed, be reduced in bulk by mixing and quartering, and duplicate samples of at least 1 quart in size be preserved for analysis.

(7) Tanning Liquors:

The liquor shall be mixed by plunging or other effective means till homogeneous and then samples of at least 1 pint be taken for analysis. The addition of 0.03 per cent. of thymol or other suitable anti-ferment to the sample is essential to keep the liquor from altering its original condition.

When routine samples are taken from day to day and a composite sample analyzed, samples of equal size shall be taken from each vat after thorough mixing, be preserved in covered containers in as cool a place as possible, and be kept from fermentation by the addition of suitable anti-ferment, as above. This bulk shall be mixed till homogeneous and samples of not less than 1 pint each be preserved for analysis.

When a sample is taken by a member of this Association in accordance with the above method, it is requested that he state upon the label of the sample submitted and upon the analysis blank that "this sample has been taken in accordance with the official method of sampling of The American Leather Chemists Association."

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Official Method for Analysis of Vegetable Tanned Leather.

(1) Preparation of Sample:

The sample of leather for analysis shall be reduced to as fine a state of division as practicable, either by cutting or grinding.

(2) Moisture:

Dry 10 grams of leather for 16 hours at a temperature between 95°-100° C.

(3) Fats:

Extract 5 to 10 grams of air-dry leather in a Soxhlet apparatus until free from grease, using petroleum ether boiling below 80° C. Evaporate off the ether and dry to approximately constant weight.

Or, if preferred, extract 30 grams of leather as described above. In the latter case, the extracted leather, when freed of solvent may be used for the determination of water-soluble material.

(4) Ash:

Incinerate 10 to 15 grams of leather in a tared dish at a dull red heat until carbon is consumed. If it is difficult to burn off all the carbon, treat the ash with hot water, filter through an ash-less filter, ignite filter and residue. Add the filtrate, evaporate to dryness and ignite.

(5) Water-Soluble Material:

Digest 30 grams of leather in a percolator over night, then extract with water at 50° C. for 3 hours. The total volume of solution to be 2 liters. Determine total solids and non-tannins according to the Official Method for extract analysis.

(6) Glucose:

Solutions.

Copper Sulphate.—Dissolve 34.639 grams of $CuSO_4.5H_2O$ in distilled water and dilute to 500 cc. Filter through asbestos.

Alkaline Tartrate Solution.—Dissolve 173 grams of Rochelle salt and 50 grams NaOH in water and dilute to 500 cc. Allow to stand 2 days and filter through asbestos.

Normal Lead Acetate Solution.—Prepare a saturated solution of normal lead acetate.

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Determination.

Place 200 cc. of leather extract of analytical strength in a ½-liter flask, add 25 cc. of a saturated solution of normal lead acetate, shake frequently (5-10 minutes), and filter. (The funnels and beakers must be kept covered to prevent evaporation.) Add to the filtrate an excess of solid potassium oxalate. Mix frequently for 15 minutes and filter, returning the filtrate until clear. Pipette 150 cc. of this filtrate into a 600 cc. Erlenmeyer flask, add 5 cc. of concentrated HCl and boil under a reflux condenser for 2 hours. Cool, neutralize (place a small piece of litmus paper in the flask) with anhydrous sodium carbonate, transfer to a 200 cc. graduated flask and make to volume. Filter through a double filter. (The filtrate must be clear.) Determine the dextrose in the solution immediately.

Place 25 cc. of the copper solution and 25 cc. of the alkaline tartrate solution in a 400 cc. beaker. Add 50 cc. of the clarified and neutralized solution above mentioned and heat to boiling in *exactly 4 minutes* and boil for 2 minutes.[1] Filter immediately without diluting, *through asbestos*,[2] wash thoroughly with hot water, then with alcohol, and finally with ether; dry for ½ hour in water oven and weigh as cuprous oxide, determine the amount of dextrose by the use of Munson and Walker's table (Bull. 107: Rev. Bu. of Chem., p. 243) and report in percentage on leather.

[1] The rate of heating of the Bunsen burner used should be regulated before sugar determinations are started. This is best done by adjusting the burner so as to bring 25 cc. copper soln. + 25 cc. alk. tartrate soln. + 50 cc. H_2O in a 400 cc. beaker to 100° C. in exactly four minutes.

[2] The finely divided, long-fibered asbestos to be used in the glucose determination should be digested with HNO_3, washed, then digested with NaOH and washed. When gooch filters are prepared, they should be washed with boiling Fehling's solution, then with HNO_3. The mats thus prepared can be used for a long time.

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MUNSON AND WALKER'S TABLE.
(Bulletin 107, Revised, Bureau of Chemistry, page 243.)
(Expressed in milligrams.)

Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)	Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)
10	8.9	4.0	55	48.9	23.5
11	9.8	4.5	56	49.7	23.9
12	10.7	4.9	57	50.6	24.3
13	11.5	5.3	58	51.5	24.8
14	12.4	5.7	59	52.4	25.2
15	13.3	6.2	60	53.3	25.6
16	14.2	6.6	61	54.2	26.1
17	15.1	7.0	62	55.1	26.5
18	16.0	7.5	63	56.0	27.0
19	16.9	7.9	64	56.8	27.4
20	17.8	8.3	65	57.7	27.8
21	18.7	8.7	66	58.6	28.3
22	19.5	9.2	67	59.5	28.7
23	20.4	9.6	68	60.4	29.2
24	21.3	10.0	69	61.3	29.6
25	22.2	10.5	70	62.2	30.0
26	23.1	10.9	71	63.1	30.5
27	24.0	11.3	72	64.0	30.9
28	24.9	11.8	73	64.8	31.4
29	25.8	12.2	74	65.7	31.8
30	26.6	12.6	75	66.6	32.2
31	27.5	13.1	76	67.5	32.7
32	28.4	13.5	77	68.4	33.1
33	29.3	13.9	78	69.3	33.6
34	30.2	14.3	79	70.2	34.0
35	31.1	14.8	80	71.1	34.4
36	32.0	15.2	81	71.9	34.9
37	32.9	15.6	82	72.8	35.3
38	33.8	16.1	83	73.7	35.8
39	34.6	16.5	84	74.6	36.2
40	35.5	16.9	85	75.5	36.7
41	36.4	17.4	86	76.4	37.1
42	37.3	17.8	87	77.3	37.5
43	38.2	18.2	88	78.2	38.0
44	39.1	18.7	89	79.1	38.4
45	40.0	19.1	90	79.9	38.9
46	40.9	19.6	91	80.8	39.3
47	41.7	20.0	92	81.7	39.8
48	42.6	20.4	93	82.6	40.2
49	43.5	20.9	94	83.5	40.6
50	44.4	21.3	95	84.4	41.1
51	45.3	21.7	96	85.3	41.5
52	46.2	22.2	97	86.2	42.0
53	47.1	22.6	98	87.1	42.4
54	48.0	23.0	99	87.9	42.9

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MUNSON AND WALKER'S TABLE.—(*Continued*)

Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)	Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)
100	88.8	43.3	150	133.2	65.9
101	89.7	43.8	151	134.1	66.3
102	90.6	44.2	152	135.0	66.8
103	91.5	44.7	153	135.9	67.2
104	92.4	45.1	154	136.8	67.7
105	93.3	45.5	155	137.7	68.2
106	94.2	46.0	156	138.6	68.6
107	95.0	46.4	157	139.5	69.1
108	95.9	46.9	158	140.3	69.5
109	96.8	47.3	159	141.2	70.0
110	97.7	47.8	160	142.1	70.4
111	98.6	48.2	161	143.0	70.9
112	99.5	48.7	162	143.9	71.4
113	100.4	49.1	163	144.8	71.8
114	101.3	49.6	164	145.7	72.3
115	102.2	50.0	165	146.6	72.8
116	103.0	50.5	166	147.5	73.2
117	103.9	50.9	167	148.3	73.7
118	104.8	51.4	168	149.2	74.1
119	105.7	51.8	169	150.1	74.6
120	106.6	52.3	170	151.0	75.1
121	107.5	52.7	171	151.9	75.5
122	108.4	53.2	172	152.8	76.0
123	109.3	53.6	173	153.7	76.4
124	110.1	54.1	174	154.6	76.9
125	110.0	54.5	175	155.5	77.4
126	111.9	55.0	176	156.3	77.8
127	112.8	55.4	177	157.2	78.3
128	113.7	55.9	178	158.1	78.8
129	114.6	56.3	179	159.0	79.2
130	115.5	56.8	180	159.9	79.7
131	116.4	57.2	181	160.8	80.1
132	117.3	57.7	182	161.7	80.6
133	118.1	58.1	183	162.6	81.1
134	119.0	58.6	184	163.4	81.5
135	119.9	59.0	185	164.3	82.0
136	120.8	59.5	186	165.2	82.5
137	121.7	60.0	187	166.1	82.9
138	122.6	60.4	188	167.0	83.4
139	123.5	60.9	189	167.9	83.9
140	124.4	61.3	190	168.8	84.3
141	125.2	61.8	191	169.7	84.8
142	126.1	62.2	192	170.5	85.3
143	127.0	62.7	193	171.4	85.7
144	127.9	63.1	194	172.3	86.2
145	128.8	63.6	195	173.2	86.7
146	129.7	64.0	196	174.1	87.1
147	130.6	64.5	197	175.0	87.6
148	131.5	65.0	198	175.9	88.1
149	132.4	65.4	199	176.8	88.5

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MUNSON AND WALKER'S TABLE.—(*Continued*)

Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)	Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)
200	177.7	89.0	250	222.1	112.8
201	178.5	89.5	251	223.0	113.2
202	179.4	89.9	252	223.8	113.7
203	180.3	90.4	253	224.7	114.2
204	181.2	90.9	254	225.6	114.7
205	182.1	91.4	255	226.5	115.2
206	183.0	91.8	256	227.4	115.7
207	183.9	92.3	257	228.3	116.1
208	184.8	92.8	258	229.2	116.6
209	185.6	93.2	259	230.1	117.1
210	186.5	93.7	260	231.0	117.6
211	187.4	94.2	261	231.8	118.1
212	188.3	94.6	262	232.7	118.6
213	189.2	95.1	263	233.6	119.0
214	190.1	95.6	264	234.5	119.5
215	191.0	96.1	265	235.4	120.0
216	191.9	96.5	266	236.3	120.5
217	192.8	97.0	267	237.2	121.0
218	193.6	97.5	268	238.1	121.5
219	194.5	98.0	269	238.9	122.0
220	195.4	98.4	270	239.8	122.5
221	196.3	98.9	271	240.7	122.9
222	197.2	99.4	272	241.6	123.4
223	198.1	99.9	273	242.5	123.9
224	199.0	100.3	274	243.4	124.4
225	199.9	100.8	275	244.3	124.9
226	200.7	101.3	276	245.2	125.4
227	201.6	101.8	277	246.1	125.9
228	202.5	102.2	278	246.9	126.4
229	203.4	102.7	279	247.8	126.9
230	204.3	103.2	280	248.7	127.3
231	205.2	103.7	281	249.6	127.8
232	206.1	104.1	282	250.5	128.3
233	207.0	104.6	283	251.4	128.8
234	207.9	105.1	284	252.3	129.3
235	208.7	105.6	285	253.2	129.8
236	209.6	106.0	286	254.0	130.3
237	210.5	106.5	287	254.9	130.8
238	211.4	107.0	288	255.8	131.3
239	212.3	107.5	289	256.7	131.8
240	213.2	108.0	290	257.6	132.3
241	214.1	108.4	291	258.5	132.7
242	215.0	108.9	292	259.4	133.2
243	215.8	109.4	293	260.3	133.7
244	216.7	109.9	294	261.2	134.2
245	217.6	110.4	295	262.0	134.7
246	218.5	110.8	296	262.9	135.2
247	219.4	111.3	297	263.8	135.7
248	220.2	111.8	298	264.7	136.2
249	221.2	112.3	299	265.6	136.7

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MUNSON AND WALKER'S TABLE.—(*Continued*)

Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)	Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)
300	266.5	137.2	350	310.9	162.4
301	267.4	137.7	351	311.8	162.9
302	268.3	138.2	352	312.7	163.4
303	269.1	138.7	353	313.6	163.9
304	270.0	139.2	354	314.4	164.4
305	270.9	139.7	355	315.3	164.9
306	271.8	140.2	356	316.2	165.4
307	272.7	140.7	357	317.1	166.0
308	273.6	141.2	358	318.0	166.5
309	274.5	141.7	359	318.9	167.0
310	275.4	142.2	360	319.8	167.5
311	276.3	142.7	361	320.7	168.0
312	277.1	143.2	362	321.6	168.5
313	278.0	143.7	363	322.4	169.0
314	278.9	144.2	364	323.3	169.6
315	279.8	144.7	365	324.2	170.1
316	280.7	145.2	366	325.1	170.6
317	281.6	145.7	367	326.0	171.1
318	282.5	146.2	368	326.9	171.6
319	283.4	146.7	369	327.8	172.1
320	284.2	147.2	370	328.7	172.7
321	285.1	147.7	371	329.5	173.2
322	286.0	148.2	372	330.4	173.7
323	286.9	148.7	373	331.3	174.2
324	287.8	149.2	374	332.2	174.7
325	288.7	149.7	375	333.1	175.3
326	289.6	150.2	376	334.0	175.8
327	290.5	150.7	377	334.9	176.3
328	291.4	151.2	378	335.8	176.8
329	292.2	151.7	379	336.7	177.3
330	293.1	152.2	380	337.5	177.9
331	294.0	152.7	381	338.4	178.4
332	294.9	153.2	382	339.3	178.9
333	295.8	153.7	383	340.2	179.4
334	296.7	154.2	384	341.1	180.0
335	297.6	154.7	385	342.0	180.5
336	298.5	155.2	386	342.9	181.0
337	299.3	155.8	387	343.8	181.5
338	300.2	156.3	388	344.6	182.0
339	301.1	156.8	389	345.5	182.6
340	302.0	157.3	390	346.4	183.1
341	302.9	157.8	391	347.3	183.6
342	303.8	158.3	392	348.2	184.1
343	304.7	158.8	393	349.1	184.7
344	305.6	159.3	394	350.0	185.2
345	306.5	159.8	395	350.9	185.7
346	307.3	160.3	396	351.8	186.2
347	308.2	160.8	397	352.6	186.8
348	309.1	161.4	398	353.5	187.3
349	310.0	161.9	399	354.4	187.8

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MUNSON AND WALKER'S TABLE.—(*Continued*)

Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)
400	355.3	188.4
401	356.2	188.9
402	357.1	189.4
403	358.0	189.9
404	358.9	190.5
405	359.7	191.0
406	360.6	191.5
407	361.5	192.1
408	362.4	192.6
409	363.3	193.1
410	364.2	193.7
411	365.1	194.2
412	366.0	194.7
413	366.9	195.2
414	367.7	195.8
415	368.6	196.3
416	369.5	196.8
417	370.4	197.4
418	371.3	197.9
419	372.2	198.4
420	373.1	199.0
421	374.0	199.5
422	374.8	200.1
423	375.7	200.6
424	376.6	201.1
425	377.5	201.7
426	378.4	202.2
427	379.3	202.8
428	380.2	203.3
429	381.1	203.8
430	382.0	204.4
431	382.8	204.9
432	383.7	205.5
433	384.6	206.0
434	385.5	206.5
435	386.4	207.1
436	387.3	207.6
437	388.2	208.2
438	389.1	208.7
439	390.0	209.2
440	390.8	209.8
441	391.7	210.3
442	392.6	210.9
443	393.5	211.4
444	394.4	212.0
445	395.3	212.5
446	396.2	213.1
447	397.1	213.6
448	397.9	214.1
449	398.8	214.7
450	399.7	215.2
451	400.6	215.8
452	401.5	216.3
453	402.4	216.9
454	403.3	217.4
455	404.2	218.0
456	405.1	218.5
457	405.9	219.1
458	406.8	219.6
459	407.7	220.2
460	408.6	220.7
461	409.5	221.3
462	410.4	221.8
463	411.3	222.4
464	412.2	222.9
465	413.0	223.5
466	413.9	224.0
467	414.8	224.6
468	415.7	225.1
469	416.6	225.7
470	417.5	226.2
471	418.4	226.8
472	419.3	227.4
473	420.2	227.9
474	421.0	228.5
475	421.9	229.0
476	422.8	229.6
477	423.7	230.1
478	424.6	230.7
479	425.5	231.3
480	426.4	231.8
481	427.3	232.4
482	428.1	232.9
483	429.0	233.5
484	429.9	234.1
485	430.8	234.6
486	431.7	235.2
487	432.6	235.7
488	433.5	236.3
489	434.4	236.9
490	435.3	237.4

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(7) Nitrogen:

Gunning modification of the Kjeldahl Method, A. O. A. C. Bulletin, No. 107 (1907).

Reagents.

Standard Acid Solutions.—Hydrochloric or sulphuric acid, the absolute strength of which has been accurately determined. For ordinary work half-normal acid is recommended. For work in determining very small amounts of nitrogen, tenth-normal is recommended. In titrating mineral acid against hydroxide solution use cochineal as indicator.

Standard Alkali Solution.—The strength of this solution relative to the acid must be accurately determined; tenth-normal solution is recommended.

Sulphuric Acid.—The sulphuric acid used should have a specific gravity of 1.84 and be free from nitrates and also from ammonium sulphate.

Sodium Hydroxide Solution.—A saturated solution of sodium hydroxide free from nitrates.

Potassium Sulphate.—This reagent should be pulverized before using.

Indicator.—A solution of cochineal is prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cc. of strong alcohol and 200 cc. of distilled water for a day or two at ordinary temperature; the filtered solution is employed as indicator.

Determination.

Place 0.7 gram leather in a digestion flask. Add 10 grams powdered potassium sulphate and from 15 to 25 cc. (ordinarily about 20 cc.) of concentrated sulphuric acid. Place the flask in an inclined position and heat below the boiling point of the acid from 5 to 15 minutes or until frothing has ceased (a small piece of paraffine may be added to prevent extreme foaming).

Then raise the heat and boil briskly until the liquid has become quite clear and nearly colorless (the digestion should take from 4 to 5 hours.

After cooling, dilute with about 200 cc. of water. Next add 50 cc. soda solution, or sufficient to make the reaction strongly

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alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 cc. will generally contain all the ammonia. The operation usually requires from 40 minutes to 1½ hours. The distillate is then titrated with standard alkali.

Previous to use, the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates present that otherwise might escape notice.

Provisional Method for the Analysis of One-Bath Chrome Liquors.

Chrome Determination.

Dilute a measured quantity of the liquor with water to a definite volume so that the dilution contains from 0.15 to 0.25 per cent. of Cr_2O_3. To 10 cc. of this dilution in a 300 cc. Erlenmeyer flask add about 50 cc. of water and about 2 grams of sodium peroxide. Boil gently 30 minutes, adding water if necessary to keep the volume from falling below about 15 cc. Cool, neutralize with strong HCl and add 5 cc. excess. Cool again. Add 10 cc. of a 10 per cent. solution of potassium iodide. After 1 minute run in from a burette 0.1 N sodium thiosulphate until the iodine color has nearly disappeared; then add a few cc. of starch solution (1 gram per liter) and titrate to the disappearance of the blue. One cc. of 0.1 N thiosulphate is equivalent to 0.002533 gram Cr_2O_3.

Acid Determination.

Place 50 cc. of the above dilution in a 7-inch porcelain dish, add about 400 cc. of water and 1 cc. of a 5 per cent. solution of phenolphthalein and bring to a boil. While boiling, titrate with 0.5 N NaOH until the pink color persists after 1 minute boiling. One cc. 0.5 N NaOH is equivalent to 0.02002 gram SO_3, 0.02452 gram H_2SO_4, 0.01773 gram Cl or 0.01823 gram HCl.

Basicity.

The basicity is the ratio of basic radical to acid radical, found by dividing the percentage of Cr_2O_3 by the percentage of SO_3 or of Cl, carrying the quotient to two decimal places.

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Provisional Method for the Analysis of Chrome Leather.

Chrome Determination.

(a) Ash 3 grams of leather. Mix the ash well with 4 grams of a mixture of equal parts of sodium carbonate, potassium carbonate and powdered borax glass and fuse for 30 minutes. Dissolve the cooled fusion in hot water with enough HCl to make the solution acid. Filter. If there is any residue on the filter, ash it and treat the ash with 1 gram of the fusion mixture in the same manner as the original ash, adding the solution to the first. Make up to 500 cc. To 100 cc. of this solution in an Erlenmeyer flask, add 5 cc. HCl and determine Cr_2O_3 as above in the analysis of one-bath chrome liquors.

(b) If it is not desired to determine Fe or Al, the ash of 3 grams of leather may be transferred to an iron crucible, mixed with 3 grams of sodium peroxide and fused 10 minutes. Place cooled crucible in 300 cc. water in a casserole and boil 20 minutes. Wash into a 500 cc. flask, cool and make up to the mark. Filter through a dry filter. Place 100 cc. of filtrate in Erlenmeyer, neutralize with HCl, add 5 cc. excess and proceed as in (a).

Provisional Method for Sulphonated Oils.

Moisture.

Weigh between 30 and 40 grams (depending on amount of water present) into a flask of 250 to 300 cc. and add 75 cc. water saturated xylol, prepared by heating a mixture of water and xylol with frequent shaking and subsequently removing the water in a separatory funnel. Connect to a Liebig condenser and place flask in a bath of paraffine or a heavy lubricating oil. Distil moderately until the distillate comes clear. Collect distillate in a tube graduated to 1/10 cc. and wash condenser with a stream of xylol from a wash bottle. Place graduated tube in hot water and when the distillate is clear, cool. The percentage of moisture is obtained by dividing the volume of water in the distillate by the weight of oil taken.

Note.—For the graduated tube Eimer & Amend's No. 3812 is recommended.

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Ash.

Weigh any convenient quantity into a dish or crucible. Ignite gently, allowing the oil to burn and complete incineration until all carbon is consumed.

Non-Saponifiable.

Weigh approximately 10 grams of oil into an 8-ounce Erlenmeyer flask and add 5 cc. aqueous KOH solution (50 grams KOH in water and dilute to 100 cc.), 45 cc. ethyl alcohol and a few glass beads. Boil 1 hour with reflux condenser. Add 100 cc. water and cool. Transfer to separatory funnel and shake at least three times with petrolic ether (B. P. 40° to 75° C.) using 50 cc. each time. Wash ether layer at least three times with 50 cc. water containing 10 cc. ethyl alcohol. Use alcohol to break emulsion. Evaporate ether extract in tared vessel, cool and weigh.

NOTE.—If the contents of the flask bump violently during saponification add 25 cc. petrolic ether, and proceed.

Combined SO_3.

(a) Weigh approximately 4 grams into an Erlenmeyer flask and boil for 40 minutes with 30 cc. HCl (1 : 5). Shake frequently. Cool, transfer to separatory funnel and shake out with petrolic ether. Draw off aqueous layer and wash ethereal layer with water. Combine washings with main aqueous portion and the sulphuric acid determine as barium sulphate. From the amount thus found, the quantity as determined in (b) is subtracted and the difference calculated as SO_3.

(b) Dissolve 4 grams in ether and shake out several times with 25 cc. concentrated brine free from sulphates. Combine the washings, dilute, filter and determine the sulphuric acid as barium sulphate.

Total Fatty Oil.

The total fatty oil shall be the difference between 100 per cent. and the sum of moisture, ash and non-saponifiable.

NOTE.—The results obtained by these methods shall be reported only in one decimal place.

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Provisional Method for Analysis of Moellons.

Moisture.

Weigh accurately 3 grams of the sample in a wide platinum dish, and heat with a low flame until the moisture is all driven off. This point can be determined by the appearance of smoke, and a slight crackling sound. Place the dish in a desiccator, cool and weigh.

Ash.

Ash the moellon remaining in the dish after the moisture determination in the usual manner, cool and weigh.

Unsaponifiable.

Weigh accurately in a 300 cc. flask, 5 grams of the moellon, add 2.5 grams caustic potash dissolved in a little water (or 5 cc. of a 50 per cent. KOH solution), and 25 cc. of 95 per cent. alcohol, boil with reflux condenser for 1 hour, shaking occasionally. Glass beads may be used to prevent bumping. Add 50 cc. hot water, cool, transfer to a separatory funnel, and extract three times, using 40 cc. petroleum ether for each extraction. A little alcohol may be added to break persistent emulsions. Wash the combined ether solutions three times with a mixture of 30 cc. of water and 10 cc. of alcohol, transfer to a tared dish, evaporate to dryness, cool and weigh. Excessive drying must be avoided.

Oxidized Fatty Acids.

Boil the soap solution remaining from the unsaponifiable determination until all the alcohol is expelled, then dissolve in hot water, transfer to a separatory funnel, rinse the beaker thoroughly into the funnel, bringing volume to approximately 300 cc., and immediately add a slight excess of concentrated HCl (about 25 per cent. more than sufficient to neutralize total alkali). Rotate the contents of the flask vigorously, cool and shake out with petroleum ether. Run off the aqueous layer, and pour off the ether layer, avoiding any loss of oxidized fatty acids. Wash these acids twice with small quantities of petroleum ether and hot water; dissolve in warm 95 per cent. alcohol, filter if necessary, transfer to a tared dish, and place in an ordinary evaporator and dryer for 16 hours; then cool and weigh. The entire operation should be conducted without delay.

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Free Fatty Acids.

Weigh out 1 gram moellon, dissolve in mixture of 20 cc. alcohol and 20 cc. sulphuric ether, which has been neutralized to phenolphthalein, and titrate with N/10 NaOH, using phenolphthalein as indicator. Test for mineral acids or alkalies (by adding methyl orange to the water emulsion of the moellon), and if present, make the necessary correction.

PROVISIONAL METHOD FOR ANALYSIS OF HARD GREASES.

Titer Test.

Saponify 75 grams of fat in a metal dish with 60 cc. of 30 per cent. sodium hydroxide (36° Bé.) and 75 cc. of 95 per cent. by volume alcohol or 120 cc. of water. Boil to dryness with constant stirring to prevent scorching, over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water and if alcohol has been used boil for 40 minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc. of 30 per cent. sulphuric acid (25° Bé.) to free fatty acids and boil until they form a clear, transparent layer. Wash with boiling water until free from sulphuric acid, collect in a small beaker, and place on the steam bath until the water has settled and the fatty acids are clear; then decant them into a dry beaker, filter, using hot water funnel, and dry 20 minutes at 100° C. When dried, cool the fatty acids to 15° or 20° C. above the expected titer and transfer to the titer tube, which is 25 mm. in diameter and 100 mm. in length (1x4 inches and made of glass about 1 mm. in thickness. Place in a 16-ounce saltmouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2.8x6 inches), fit it with a cork, which is perforated so as to hold the tube rigidly when in position. Suspend the thermometer, graduated to 0.10° C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains stationary for 30 seconds. Then allow the thermometer to hang quietly, with the bulb in the center of the mass, and observe the rise of the mercury. The highest point to which it rises is recorded as the titer of the fatty acids.

Test the fatty acids for complete saponification as follows:

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Place 3 cc. in a test-tube and add 15 cc. of alcohol (95 per cent. by volume). Bring the mixture to a boil and add an equal volume of ammonium hydroxide (0.96 sp. gr.). A clear solution should result, turbidity indicating unsaponified fat. The titer must be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

Unsaponifiable.

Same as for Unsaponifiable in Moellons.

Free Fatty Acids.

Same as for Free Fatty Acids in Moellons.

PROVISIONAL METHOD FOR ANALYSIS OF LACTIC ACID.

Free Sulphuric Acid.

Dissolve 50 grams of the sample in 200 cc. alcohol, which should be neutral, and of at least 95 per cent. strength. Heat to 60° C., cover and let stand over night in a warm place. Filter off precipitated material and wash with alcohol. Evaporate off the alcohol, make up residue to 250 cc. with water, add 5 cc. strong HCl, boil, add $BaCl_2$ and determine $BaSO_4$ in the usual way. Calculate to per cent. H_2SO_4 on the original sample.

Volatile Acid.

Weigh out 1 gram of sample, make up to about 50 cc. with water, titrate with 0.5 N NaOH. Calculate the result to lactic acid: (1 cc. 0.5 N NaOH = 0.045 gram lactic acid.) On this basis, make up a solution containing about 15 grams of acid per liter. Place 150 cc. of this dilution in a long-necked 300 cc. Kjeldahl flask, connected through a Kjeldahl bulb trap to a vertical spiral condenser, the total height from the bottom of the flask to the top of the turn connecting with the condenser being between 20 and 24 inches. Distil over 125 cc. in from 47 to 53 minutes, counting from the time the first drop falls into the receiver, which should be a graduated cylinder. Add 125 cc. of water to the residue in the flask and repeat. Titrate both distillates with 0.1 N NaOH and phenolphthalein and calculate result

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to grams of acetic acid: 1 cc. 0.1 N NaOH = 0.006 gram acetic acid. From these figures for acid found in distillates find actual

TABLE SHOWING THE RELATION OF AMOUNTS OF VOLATILE ACID FOUND IN DISTILLATE OBTAINED UNDER STANDARD CONDITIONS TO THE AMOUNTS ACTUALLY PRESENT IN DISTILLING FLASK, IN MILLIGRAMS.

One Distillation.

In distillate	In flask	In distillate	In flask	In distillate	In flask	In distillate	In flask
1	0.0	14	17.5	27	37.5	40	57.9
2	0.0	15	19.0	28	39.0	41	59.6
3	0.0	16	20.5	29	40.6	42	61.3
4	2.0	17	22.1	30	42.1	43	62.9
5	3.5	18	23.6	31	43.7	44	64.6
6	5.1	19	25.2	32	45.2	45	66.3
7	6.7	20	26.7	33	46.8	46	68.0
8	8.2	21	28.2	34	48.3	47	69.8
9	9.8	22	29.8	35	49.9	48	71.5
10	11.3	23	31.3	36	51.5	49	73.3
11	12.8	24	32.9	37	53.1	50	75.0
12	14.4	25	34.4	38	54.7	51	76.8
13	15.9	26	35.9	39	56.3	52	78.5

Two Distillations.

5	0.0	22	19.2	39	38.9	56	58.6
6	1.0	23	20.4	40	40.0	57	59.8
7	2.0	24	21.5	41	41.1	58	61.1
8	3.0	25	22.7	42	42.3	59	62.3
9	4.0	26	23.9	43	43.4	60	63.5
10	5.0	27	25.0	44	44.6	61	64.7
11	6.2	28	26.2	45	45.7	62	65.9
12	7.4	29	27.3	46	46.8	63	67.2
13	8.6	30	28.5	47	48.0	64	68.4
14	9.8	31	29.7	48	49.2	65	69.6
15	11.0	32	30.8	49	50.3	66	70.8
16	12.1	33	32.0	50	51.5	67	72.0
17	13.4	34	33.1	51	52.7	68	73.3
18	14.5	35	34.3	52	53.9	69	74.5
19	15.7	36	35.4	53	55.0	70	75.7
20	16.9	37	36.6	54	56.2	71	76.9
21	18.1	38	37.7	55	57.4	72	78.1

weight of volatile acid placed in boiling flask, by means of table, and calculate this result to percentage of volatile acid in the sample.

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Free Acid and Anhydride.

Titrate 50 cc. of the dilution made up for volatile acid, in the cold, with 0.5 N NaOH and phenolphthalein to first full pink. Call this figure "first titration." From it subtract a number of cc. of 0.5 N NaOH equivalent to the sum of volatile acid and free sulphuric acid present in the 50 cc. of dilution. (If the sample contains free oxalic or hydrochloric acid, the amount must be determined by appropriate methods, and further deduction made.) Calculate the remainder to lactic acid and express it as a percentage of the sample. This is the free lactic acid. After completing the first titration, add 4 cc. excess alkali, or in the case of concentrated acids 5 cc., and stand aside at room temperature (20-25° C.), for 15 minutes. Then add 5 cc. 0.5 N H_2SO_4, boil, and titrate back with 0.5 N NaOH. The amount of alkali used by anhydride is now found by subtraction and calculated to lactic acid. Express this as per cent. of lactic acid equivalent to anhydride present in sample.

OFFICIAL FORM FOR THE REPORTING OF EXTRACT ANALYSIS.

Analysis.

Tannin.....	Total Solids.....
Non-tannins.....	Soluble Solids.....
Insolubles.....	Ash .....
Water.....	Specific Gravity.....
Total.....	Twaddell .....

Analyzed by the Official Method of the A. L. C. A. { SLOWLY / RAPIDLY } Cooled.

IRON TANNAGE.

By Daniel D. Jackson and Te Pang Hou.

[*Continued from page 75*]

SECTION III. INVESTIGATION OF DIFFERENT METHODS OF OXIDATION AND SOME METHODS OF PREPARATION OF IRON LIQUOR FROM COPPERAS.

As the largest and cheapest commercial source of iron salts is in the form of the ferrous sulphate or "copperas," $FeSO_4.7H_2O$, this particular salt of iron naturally forms the starting point for the preparation of the tanning solutions. As the ferric salts are

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generally more expensive than the corresponding ferrous salts, economy demands that the iron tanning liquor shall be made from the ferrous salt—"copperas" in particular—rather than directly from a ferric salt purchased as such. Hence it is clear that a proper method of oxidation is essential to the preparation of this tanning liquor and constitutes one of the main factors in the economic aspects of iron tannage. Consequently it is worth while to devote some attention to the study of different methods of oxidation and of the value of different oxidizing agents from the tanning point of view. In this investigation, mostly qualitative, we have constantly kept in view three points, namely (1) the simplicity of the method by which oxidation can be carried out; (2) the character (acidity, etc.) of the liquor thus obtained in regard to the convenience for use; and (3) the cheapness of the chemicals employed. In the following there is given a brief summary of the properties and behavior towards ferrous sulphate solution of some of the more important oxidizing agents, although the study includes practically all of the ordinary oxidizing agents available.

Sodium Dichromate, $Na_2Cr_2O_7.2H_2O$.—Oxidation goes on in the cold and to completion (as tested with $K_3Fe(CN)_6$ solution) even in the absence of any acid added. There is a tendency for the ferric oxide, $Fe_2O_3.xH_2O$, to separate out. With a small amount of a mineral acid added no precipitate will be formed and the reaction is distinctly accelerated by the higher hydrogen-ion concentration.

$$Cr_2O_7^{=} + 6Fe^{++} + 14H^{+} \rightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O.$$

This method is an important one and embodies one mode of tannage found to give satisfactory results. It has several advantages: (1) that the oxidation reaction requires only a very low hydrogen-ion concentration, so that the acidity of the liquor obtained is entirely in control; (2) that the oxidation potential is high and the oxidation reaction is completed very smoothly in the cold; and (3) that the waste product, Cr^{+++} salts left in the resulting liquor is itself a valuable tanning agent and constitutes what may be called a co-tanning agent with the iron. Furthermore, a slight excess of the sodium dichromate in the liquor could effectively prevent any ferric iron from being reduced to

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the ferrous state in the course of tanning. In spite of the present high price of the dichromate, the process has merits of its own as will be presented in detail in a later section.

Sodium Chlorate, $NaClO_3$.—The oxidation by a chlorate $NaClO_3$ or $KClO_3$ in a cold solution does not occur without the addition of a mineral acid (HCl or H_2SO_4). On adding the acid the reaction takes place rapidly and goes to completion in the cold. The solution assumes a greenish-yellow color, probably due to some chlorine dioxide formed, ClO_2.

$$2NaClO_3 + HCl \longrightarrow 2NaCl + HClO_3.$$
$$HClO_3 + 6FeSO_4 + 5HCl \longrightarrow 2Fe_2(SO_4)_3 + 2FeCl_3 + 3H_2O.$$
$$3HClO_3 \longrightarrow H_2O + 2ClO_2 + HClO_4.$$

With a weaker acid, like acetic acid, oxidation takes place on heating, giving a red solution due to the formation of the basic ferric salt. Without any acid added the reaction can be brought about by heating, but $Fe_2O_3.xH_2O$ would then be thrown down. As the chlorate is rather expensive, especially the potassium chlorate, the process will not be economical, although W. Mensing advocated its use in his patent.[15]

Manganese Dioxide, MnO_2.—In the absence of any acid, no reaction takes place, MnO_2 being insoluble. On adding HCl, evolution of Cl_2 gas is observed and the solution turns yellowish, this being the characteristic color of the ferric chloride in solution.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2.$$

The reaction proceeds to completion in the cold.

If in place of HCl, H_2SO_4 is used, the yellow color does not develop. The reaction goes to completion only when a large excess of MnO_2 and H_2SO_4 is employed. A small but distinct amount of the permanganate is formed when all ferrous iron has been oxidized. Hence if MnO_2 is to be employed as the oxidizing agent, HCl rather than H_2SO_4 should be used. Molac and Friedel in 1855 prepared their iron liquor from ferrous sulphate with MnO_2 and H_2SO_4.

Nitric Acid, HNO_3.—1. *HNO_3* alone.[16] Dilute HNO_3 has scarcely any oxidizing action upon a dilute $FeSO_4$ solution in

[15] Swiss Patent No. 75,775, Class 40, February 1, 1918.

[16] This method was used by Knapp, but the liquor he prepared yielded much $Fe_2O_3.xH_2O$.

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the cold. With somewhat more concentrated HNO_3 solution, a black coloration gradually develops due to the reduction of some HNO_3 to nitric oxide, NO, which unites with $FeSO_4$ to form the ferrous nitroso compound $FeSO_4.NO$. The black color deepens on warming and persists even on boiling if the concentration of the HNO_3 in the solution is not high enough to effect the oxidation. With the addition of more HNO_3 or with an increase in the concentration of the HNO_3 due to the loss of water by prolonged boiling, complete oxidation finally takes place and all of the nitroso compound is decomposed. The solution then boils violently, brown fumes of nitrogen dioxide, NO_2, being given off. During the evolution of the gas the temperature of the solution falls 4° or 5° C. The amount of HNO_3 required for complete oxidation depends largely upon the concentration rather than the absolute quantity of HNO_3 present. Starting with a saturated solution of $FeSO_4.7H_2O$ (one part of $FeSO_4.7H_2O$ in about one and a half parts of water by weight) and using 1.42 HNO_3, a considerably less amount of the HNO_3 need be employed, but 25 per cent. of 1.42 HNO_3 of the weight of $FeSO_4.7H_2O$ taken is found to be the working minimum under such conditions. Although complete oxidation can still be brought about with a less quantity, say 20 per cent., the liquor obtained becomes too alkaline and has a muddy appearance, due to the separation of the ferric oxide. This can be readily understood when we see that when the ferrous salt is oxidized to the ferric salt, the solution becomes less acid and the greater part of the HNO_3 used simply goes to furnish the necessary acidity (see paragraph under $HNO_3 + H_2SO_4$ below). Some HNO_3 is lost by boiling.

The oxidation of the ferrous iron to the ferric state by HNO_3 in the *cold* can only approach completion when a very large excess of the concentrated HNO_3 is added to a concentrated ferrous sulphate solution. Consequently boiling is a necessary operation which makes the process less simple, as boiling nitric acid solution requires a special container to resist corrosion.

2. $HNO_3 + H_2SO_4$. As was said above, the oxidation of the ferrous solution to the ferric state renders the solution more alkaline, so that an acid must be added to prevent any ferric salt from being hydrolyzed and precipitated. If H_2SO_4 in the re-

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quired amount is added to supply the acidity, the HNO_3 needed can be cut down from 25 per cent. of the weight of the $FeSO_4.7H_2O$ to 9.5 per cent.. Thus—

$$3FeSO_4.7H_2O + 4HNO_3 \rightarrow 3Fe(NO_3)(SO_4) + NO + 2H_2O$$

theoretically requires 30.2 per cent. HNO_3 of $FeSO_4.7H_2O$.

$$6FeSO_4.7H_2O + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

theoretically requires only 7.55 per cent. HNO_3 of $FeSO_4.7H_2O$. As HNO_3 is far more expensive than H_2SO_4 this method is more economical.

3. *$H_2SO_4 + NaNO_3$*.[17]—With a saturated ferrous sulphate solution (1 part $FeSO_4.7H_2O$ in about 1½ parts of water) and with 25 per cent. of H_2SO_4 and $NaNO_3$ each in excess calculated according to the following reaction,

$$6FeSO_4.7H_2O + 4H_2SO_4 + 2NaNO_3 \rightarrow 3Fe_2(SO_4)_3 + Na_2SO_4 + 2NO + 4H_2O,$$

the reaction goes on very smoothly by continued boiling. The resulting liquor, thick like a syrup and dark red in color, has a specific gravity as high as 1.50 — 1.55 and contains iron as $Fe_2(SO_4)_3$ from 40-45 per cent. As Chile saltpetre, $NaNO_3$, is much cheaper than HNO_3, this method is still more economical. Furthermore, the Na_2SO_4 formed in the liquor cuts down the amount of NaCl needed for tanning. Taking 4-5 per cent. as the normal figure for NaCl used on the weight of the pelt, this saves about 25 per cent. of NaCl required.

4. *$HNO_3 + HCl$,* aqua regia.—The reaction starts in the cold. When only a small quantity is added to the ferrous sulphate solution the black color of the nitroso compound is observed, but on further addition of aqua regia the nitroso compound is decomposed and the reaction goes to completion, although the end-point is not very permanent. The solution on standing gradually assumes a golden yellow color due to some hypochlorous anhydride Cl_2O formed. The main reactions seem to be—

$$HNO_3 + 3HCl \rightarrow NOCl + Cl_2 + 2H_2O,$$
$$NOCl + Cl_2 + 3FeSO_4 \rightarrow NO + FeCl_3 + Fe_2(SO_4)_3,$$

although other oxidizing agents such as HNO_2 and HClO are

[17] This method was used by Knapp, but the details differ.

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also formed. The proportion of 1.20 HCl to 1.42 HNO_3 is 3—3.5 to 1 by volume of the concentrated solutions.

The oxidizing power of aqua regia seems to be greater than that of the concentrated HNO_3 alone, but some assert that there is no difference in oxidation potential between aqua regia and concentrated nitric acid.[18] As aqua regia is difficult to handle and rapidly corrodes the container, this method of oxidation is neither economical nor simple.

It will be noticed that with the possible exception of $HNO_3 +$ HCl, all methods involving oxidation by HNO_3 in some form require a boiling temperature. This constitutes a very unfortunate feature. There are, however, some distinct advantages in the case of $NaNO_3 + H_2SO_4$, *viz.*, (1) that the materials used are cheap; (2) that a very concentrated liquor can be obtained, and (3) that with a proper amount of H_2SO_4 employed the liquor obtained is stable and there is no danger of deterioration on storing.

Chlorine Gas, Cl_2.—The oxidation by chlorine is very smooth and simple. The reaction starts in the cold and goes to completion when the gas is passed in under a small pressure and when efficient stirring is maintained. The reaction furnishes its own acidity and in the right proportion.

$$Cl_2 + H_2O \longrightarrow HCl + HClO.$$
$$HClO + FeSO_4 + HCl \longrightarrow FeCl.(SO_4) + H_2O.$$

The process is very efficient and incurs practically no loss of Cl_2 if two or three units are connected in series and the solutions treated countercurrently. Iron liquor obtained by this method is of course saturated with Cl_2 and so contains a slight excess of it, but this is indeed an advantage for it prevents the ferric salt from being reduced again and also enables the liquor to be kept in storage without any danger of deterioration, *i. e.*, either $Fe_2O_3 \cdot xH_2O$ separating out or some ferric salt changing to the ferrous. As liquid chlorine now can be obtained in large quantities and at a reasonable cost, there is in it much to recommend from a commercial standpoint.

Bleaching Powder, CaCl.ClO.—This method is one of the first used by us in this research. The oxidation goes on in the cold.

[18] Moore, "Aqua Regia," *J. A. C. S.*, p. 1091 (1911), and "Aqua Regia II," *J. A. C. S.*, p. 33 (1913).

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With large excess it is possible to oxidize completely the ferrous iron without adding any acid, in which case a precipitate of $Fe_2O_3.xH_2O$ is liable to come down. With a weak acid present, *e. g.*, acetic acid, the reaction is accelerated, and with a mineral acid it goes to completion readily. $CaSO_4.2H_2O$ is thrown down. $Fe_2O_3.xH_2O$ is more readily separated from this liquor probably due to the greater coagulating influence of the divalent radicals. The bleach suspension itself reacts alkaline so that the addition of an acid is rendered more necessary. As the oxidizing agent is really HClO, there is no advantage in using this material over liquid chlorine and the cost is greater for the chlorine content in this form. The bleach, however, can be used to advantage in connection with iron tanning processes (to be described in later Sections).

Sodium Nitrite, $NaNO_2$.—Unlike $NaNO_3$, oxidation begins in the cold, but basic ferric salt would be precipitated when no acid is added. On adding an acid (HCl or H_2SO_4) the red precipitate redissolves and nitrogen oxide gases are rapidly given off.

$$2HNO_2 \longrightarrow H_2O + N_2O_3.$$
$$N_2O_3 \rightleftarrows NO_2 + NO.$$

The reaction then goes to completion in the cold when an excess of $NaNO_2$ is present. With acetic acid the reaction can also go to completion giving a colloidal suspension. As the $NaNO_2$ solution reacts alkaline, the addition of an acid is all the more necessary. The oxidation potential of HNO_2 is lower than that of HNO_3,[19] although the latter produces no appreciable oxidation in the *cold,* especially when the solution is dilute. Since HNO_2 is unstable and is decomposed readily, the loss of HNO_2 through decomposition and volatilization is very great. Bystron and Vietinghoff[20] patented a cyclic process to collect these gases, oxidize them all to NO_2 by air, and use the gas again for oxidation. It is probable that such a method can not be carried out in practice without undue complications.

Hydrogen Peroxide, H_2O_2.—The oxidation starts in the cold, but does not go to completion without a large excess. Even with a large excess the end-point is not stable. $Fe_2O_3.xH_2O$ is thrown

[19] Ihle, *Z. f. phys. Chem.,* Vol. 19, p. 577 (1896).

[20] German Patent No. 255,320 (1911) and a number of patents following.

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down on standing for a few minutes. The solution is red, due to the basic ferric salt formed. If an acid (HCl or H_2SO_4) is added the color of the solution becomes yellow and the reaction goes to definite completion, giving a more permanent end-point.

$$H_2O_2 + 2FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2H_2O.$$

As H_2O_2 cannot be obtained cheaply, at least at present, its use will not be commercially practicable.

Potassium Perchlorate, $KClO_4$.—The oxidation starts only on warming when no acid is added, but the solution then becomes turbid. On adding an acid, the turbidity clears up but the reaction does not go to completion even when the solution is heated to boiling. Thus contrary to what one might suppose, the oxidation potential of the perchloric acid is lower than that of the chloric acid.

Oxygen From the Air.—The oxidation of the ferrous sulphate by air oxygen would be a very cheap method if it could be brought about rapidly enough. Fine bubbles of air are passed through the ferrous sulphate solution, but the reaction is too slow, only 6 per cent. being oxidized at the end of four hours. At an elevated temperature, 80°-90° C., the reaction is more rapid, but even then only 12 per cent. is found to be oxidized in four hours. 10 per cent. concentrated H_2SO_4 of the weight of the $FeSO_4.7H_2O$ in the solution (1 part $FeSO_4.7H_2O$ to 2 parts water) should be present, otherwise ferric oxide would be precipitated. The ordinary catalytic agents, such as the mercuric salt (5 per cent. $HgCl_2$) and the phosphate (5 per cent. Na_2HSO_4) do not seem to help. Ozonized air, or air led through an electric ozonizer, would do better, but would be expensive.

Anodic Oxidation.—Oxidation by electrolysis seems to have some possibilities. The anode is best made of lead but the cathode can be lead, graphite, copper, or even iron. These materials have been tried. Lead and graphite as cathodes are inert in the acid (H_2SO_4) solution and are found to be suitable. Copper cathode is not attacked by the acid when the cells are running, but when the current is stopped it is attacked by the acid with the aid of atmospheric oxygen, thus contaminating the electrolyte. An iron cathode can be used to advantage as it is of the same material as the liquor is composed of. As the cathode environment is a

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reducing one, a diaphragm such as porous earthware, asbestos felt, or electro-filtrose should be provided to separate the cathode portion from the main electrolyte. This arrangement prevents the hydrogen gas evolved at the cathode from mixing with the main electrolyte. The cathode chamber need not be large, and a capacity of about one-fifth or less of the volume of the main electrolyte is sufficient. The cathode solution can best be a plain H_2SO_4 solution and should be maintained at a higher level than the body of the electrolyte to prevent diffusion of much iron into the chamber. It is found that the H_2SO_4 concentration inside this chamber should be maintained high, about two or three times as high as in the main electrolyte, otherwise some iron might be plated on the cathode. The electrolyte is made by dissolving copperas in about twice its weight of water and adding 15 per cent. concentrated H_2SO_4 of the weight of copperas taken. As, generally speaking, the oxygen over-voltage is low[21] oxygen gas is easily caused to be discharged at the anode, resulting in low current efficiency. To prevent this, the anode current density must be low, *i. e.*, the anode surface must be large. It is found that with the anode current density of 0.20—0.40 amperes per square decimeter for a liquor containing 25—40 per cent. of copperas, the over-all current efficiency is as high as 70—75 per cent., even when there is no circulation or stirring in the main electrolyte. With good circulation or stirring and with a concentrated electrolyte (30—40 per cent. $FeSO_4.7H_2O$) a higher current density can be safely employed without any danger of the discharge of oxygen gas at the anode. The cell takes a voltage of 2.4—3.0 volts depending upon the distance between the electrodes, the condition of the diaphragm, the concentration of the electrolyte and its temperature, but with the cells running properly and with the electrodes about 4 inches apart, this terminal potential drop should not be much over 2.6 volts under normal conditions. The back E. M. F. is approximately 2 volts. Oxidation can go to completion by this method, but the end-point is not quite permanent. As each cell on the average takes less than 3.0 volts, there can be connected in series on the 120 main about 40 cells. In this way, the method compares favorably with the cheapest chemical methods. The disadvantage seems to be that considerable amount of $Fe_2O_3.xH_2O$

[21] See Allmand, "Applied Electrochemistry," p. 144 (1920).

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is thrown down as sludge in the cells and the cells need close attention and regulation in regard to the acidity in the cathode chamber, proper conditions of the diaphragm, etc., otherwise secondary reactions might set in and the cells fail to function properly. It is found that the lead anode is oxidized only after all iron has been oxidized.

From the above brief description it will be seen that, to produce such a cheap product as the ferric salt, many of the costly and rarer oxidizing agents will find no place. Considerations of the different factors point, for the present at least, to the methods oxidation by chlorine, oxidation by $NaNO_3$ and H_2SO_4, oxidation by HNO_3 and H_2SO_4, and oxidation by $Na_2Cr_2O_7$ utilizing the chrome. The other methods that possess some possibilities are anodic oxidation and oxidation by the atmospheric oxygen in some form, while oxidation by $NaClO_3$ or other chlorate, oxidation by $NaNO_2$, and oxidation by MnO_2 and HCl seem to have a doubtful economic value.

The details of a few methods of preparation of the iron liquor, which have been found suitable, will now be given. They are based on the oxidation by (I) liquid chlorine, (II) sodium nitrate and sulphuric acid, (III) nitric acid and sulphuric acid, and (IV) sodium dichromate. Liquid chlorine, as far as we know, has never been used before. While sodium nitrate and nitric acid used for oxidation in conjunction with sulphuric acid are more or less well known[22] the details of procedure in regard to the proportions of the materials employed, the concentration aimed at and acidity desired, etc., are worked out independently. The conditions as given here are those found capable of producing (1) a high concentration of iron in the liquor, (2) complete oxidation of iron with some excess of the oxidizing agent in the liquor, (3) complete reaction involving the use of a minimum amount of the oxidizing agent and other materials, and (4) a degree of acidity as near that suitable for tanning operation as possible, consistent with the stability of the liquor. *The one difficulty with the prepared sulphate liquor is that, unless the degree of acidity is above a certain minimum it does not keep well and ferric oxide is liable to separate out.* The separation of much ferric oxide would

[22] H_2SO_4 and HNO_3 used as early as 1842 by Bordier, and H_2SO_4 and $NaNO_3$ in 1879 by Knapp.

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greatly impair the tan liquor and this danger should always be guarded against when the liquor is to be placed on the market where its keeping quality is of vital importance.

(I) *Oxidation by Chlorine.*—For laboratory preparation. A desired weight of commercial copperas is placed in 1¼ to 1½ times its weight of water in a large container provided with an entrance and an exit hole. Through one hole is passed a delivery tube reaching to the bottom of the container. During the passage of the gas, the contents are stirred constantly. As the copperas crystals gradually disappear more can be added until the total weight of the copperas used is equal to the weight of the water present. Toward the end, the exit hole is stopped temporarily to create a small pressure of the chlorine gas above the solution. The completion of oxidation is tested with $K_3Fe(CN)_6$ solution. The end-point should be so permanent that a test sample with $K_3Fe(CN)_6$ solution should be colored deep red and remain so for at least one-half hour in contact with air.

To the liquor 35 per cent. commercial NaCl and 10 per cent. soda ash of the weight of the copperas taken are added, the latter being first dissolved in a small quantity of water and added very slowly with stirring. This liquor thus neutralized should be used without much delay. To make the liquor keep for a short period, pass in again chlorine gas under a small pressure and immediately stopper the bottle tightly. For long storage, it is safer not to add this quantity of Na_2CO_3 until ready for use. The bottle should be tightly closed so that no chlorine gas can escape. No acid need be added to the ferrous sulphate solution for chlorine oxidation.

For commercial preparation, cast iron or enameled iron tanks may be used. Two or three units sould be connected in series and the gas passed in countercurrently.

The liquor thus prepared is dark red in color, but should be absolutely clear, and should remain so without depositing yellow hydrated ferric oxide on standing. It is rather thick and, after the addition of NaCl, has a specific gravity of 1.39. It contains approximately 32 per cent. of iron calculated as $Fe_2(SO_4)_3$.

On the basis of 100 pounds of the drained pelt, the cost of preparation is estimated as follows:

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Copperas.....	14 pounds at 1¢	a pound	$0.14
Liquid chlorine.....	2 pounds at 7¢	a pound	.14
NaCl (crude).....	5 pounds at ½¢	a pound	.02½
Na_2CO_3 (comm.).....	1½ pounds at 1½¢	a pound	.02¼
		Total	$0.32¾

This will give approximately 2¾ gallons of the liquor in a concentrated form, weighing about 31 pounds. For use, dilute to 15—25 gallons for drum tannage. The cost of preparation per gallon of the concentrated liquor is estimated to be about 12 cents, or per pound a little over 1 cent.

(II) *Oxidation by* $NaNO_3$ and H_2SO_4.—For laboratory preparation. Take a desired quantity of commercial copperas and place it in a large container containing about 1½ times its weight of water to which have been added 30 per cent. of 66° Bé. H_2SO_4 and 12½ per cent. of Chile saltpetre of the weight of the copperas taken. Heat to boiling and boil gently until brown fumes of NO_2 are finally given off. Remove the burner during evolution of the gas.

Add 20 per cent. NaCl and neutralize slowly with 9½ per cent. soda ash previously dissolved in a small quantity of water. The liquor is ready for immediate use.

For Commercial Preparation. Use an enameled open kettle provided with a steam jacket taking exhaust steam. The kettle should have a somewhat larger capacity, as during evolution of the gas the liquor foams badly.

The evolution of NO_2 fumes indicates the end-point for the reaction and that a small excess of HNO_3 is present. This represents, of course, a loss in HNO_3 though small, which would otherwise be available for oxidation. But as a small excess is always necessary to carry the reaction to completion, this minor loss seems to be unavoidable.

The above proportion of $NaNO_3$ and H_2SO_4 represents an excess of 15—20 per cent. over the theoretical quantity in each. This is found to be the minimum quantity, especially in the case of $NaNO_3$, in order to secure a complete oxidation without rendering the resulting liquor too alkaline. Rather prolonged boiling is needed before NO_2 fumes are given off, as a certain concentration of HNO_3 in solution must be attained before the com-

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plete reaction can take place. But the liquor obtained is more concentrated due to the loss of water by boiling.

Before the addition of NaCl and Na_2CO_3 the liquor has a specific gravity of about 1.50 containing, in this condition, about 36 per cent. $Fe_2(SO_4)_3$. It is a thick liquid, dark red in color. It is absolutely clear and should remain so on long standing without deposition of ferric oxide.

On the basis of 100 pounds, the cost of manufacture is estimated as follows:

Copperas	14	pounds at 1¢	a pound	$0.14
H_2SO_4 (66° Bé.)	4⅛	pounds at 1¢	a pound	.04⅛
Chile Saltpetre	1¾	pounds at 3¢	a pound	.05¼
NaCl	3	pounds at ½¢	a pound	.01½
Soda ash	1½	pounds at 1½¢	a pound	.02¼
			Total	$0.27⅛

This gives approximately 2.5 gallons of the concentrated liquor weighing about 30 pounds before neutralization with soda ash. For use, dilute the liquor to 15—25 gallons for drum tannage. The cost of preparation is estimated to be about 11 cents per gallon of concentrated liquor, or about 1 cent per pound.

(III) *Oxidation by HNO_3 and H_2SO_4.*—For Laboratory Preparation. Take a desired quantity of copperas and place it in a container containing 1½ times its weight of water to which have been added 9½-10 per cent. of 1.42 HNO_3 and 19 per cent. of 66° Bé. H_2SO_4. Proceed as in (II). 35 per cent. NaCl of the weight of the copperas taken and 9½ per cent. soda ash are later added.

The use of HNO_3 alone without sulphuric acid is very expensive and wasteful.

The liquor has the same general properties as that prepared by (II).

On the basis of 100 pounds of the hide, the cost of manufacture is as follows:

Copperas	14	pounds at 1¢	a pound	$0.14
HNO_3 (1.42)	1⅓	pounds at 8¢	a pound	.20⅔
H_2SO_4 (66° Bé.)	2⅔	pounds at 1¢	a pound	.02⅔
NaCl	5	pounds at ½¢	a pound	.02½
Na_2CO_3	1⅓	pounds at 1½¢	a pound	.02
			Total	$0.31⅝

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The resulting liquor is of about the same volume as that in (II) but weighs a little less. The cost of preparation is estimated to be about 13 cents per gallon of concentrated liquor, or a little over 1 cent per pound.

(IV) *Chrome-Iron Liquor.*—For Laboratory Preparation. Take a desired quantity of copperas and place it in an equal weight of water. Add 35 per cent. of 66° Bé. H_2SO_4. Stir until as much of the copperas is dissolved as possible. Cool and add gradually, with stirring and cooling, 20 per cent. of sodium dichromate crystals of the weight of the copperas taken, and then add 30 per cent. NaCl. The liquor is ready for use without neutralization, or with but a small quantity of an alkali added.

For Commercial Preparation. The proportions and procedure hold good, except that an enameled tank or crockery should be used and cooling coils of hard lead should be provided.

Considerable heat is evolved upon the addition of H_2SO_4 and in the introduction of $Na_2Cr_2O_7.2H_2O$, so that cooling facilities should be provided in commercial work when a concentrated liquor is desired. When the liquor is made by the tanners themselves for immediate use, the following procedure can be adopted: For each 100 pounds of the drained skins, take 10 pounds of copperas in 40 pounds or 5 gallons of water, contained in crockery ware. Add 3⅕ pounds of 66° Bé. H_2SO_4, stir well and cool, and then gradually introduce 2 pounds of $Na_2Cr_2O_7.2H_2O$ with good stirring. Dilute to 15—25 gallons for drum tannage. No alkali need be added.

The liquor is rather thick and appears black, as the red color of the iron and the green of the chromic salt tend to neutralize each other. After the addition of NaCl, it has a specific gravity of 1.49 and contains about 26 per cent. iron calculated as $Fe_2(SO_4)_3$ and 8½ per cent. chromium as $Cr_2(SO_4)_3$.

On the basis of 100 pounds of drained pickled sheepskins, the cost of preparation is estimated as follows:

Copperas	10	pounds at	1¢ a pound	$0.10
H_2SO_4 (66° Bé.)	3⅕	pounds at	1¢ a pound	.03⅕
$Na_2Cr_2O_7.2H_2O$	2	pounds at	28¢ a pound	.56
NaCl	3	pounds at	½¢ a pound	.01½
			Total	$0.70⅒

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The liquor obtained in this concentrated form measures approximately 2.2 gallons and weighs 27½ pounds. The cost of preparation is about 32 cents a gallon, or 2.6 cents a pound.

This liquor is different from any of the above in that it contains a basic chromic salt as well as ferric salt, which chromic salt also contributes to the tannage. While it costs two and a half times as much as the liquor obtained by any of the first three methods, its cost is still very much less than that of a one-bath chrome liquor.

Section IV. Hydrolysis and Decomposition of Ferric and Chromic Salts Compared.

It may well be suspected that one of the reasons why iron liquor is so much more difficult to manage than chrome liquor might be found in the greater tendency of the ferric salts, particularly the sulphate, in solution to yield readily a precipitate. On the other hand, it may be appreciated why chrome liquor is advantageous when the peculiar properties of the chromic salts are recalled. Chromic salts, both the sulphate and the chloride, in solution are capable of forming "complexes." The bluish hexahydrate chromic chloride, $CrCl_3.6H_2O$, obtained from crystallization in the cold, gives a violet solution which turns green on boiling. This saturated violet solution, when treated with hydrogen chloride gas in the heat yields green crystals, the aqueous solution of which, when freshly prepared, possesses only two chlorine atoms out of the three in the molecule that are precipitable by $AgNO_3$.[23] Chromic sulphate in solution also forms "complexes." The reddish-violet crystals, $Cr_2(SO_4)_3.15H_2O$, gives a bluish violet solution in cold water which also turns green on boiling. This green compound can yield, with H_2SO_4 on warming, products whose $SO_4^=$ radical is not precipitable by $BaCl_2$.[24] The chemistry of chromic salts in solution is certainly a complex one. Certain irregularities in the behavior of a chrome liquor may possibly be due to this complex nature. As far as is known, no such peculiarities exist in the ferric salt solution.

A qualitative comparison between the behavior of a neutral ferric salt solution and a neutral chromic salt solution both in an

[23] See Ostwald, "Principles of Inorganic Chemistry," translated by A. Findlay, p. 636 (1914).

[24] *Ibid.* Also Holleman, "A Text Book of Inorganic Chemistry," translated by H. C. Cooper, p. 461 (1916).

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excessively diluted form is instructive. 1 cc. of a 10 per cent. neutral ferric sulphate solution is diluted to 100 cc. and allowed to stand for 24—36 hours. A fine precipitate of yellow hydrated ferric oxide copiously settles at the bottom. With further dilution to 300 cc. and standing, about two-thirds of the original amount of iron in solution separates out and the solution becomes so depleted that it appears almost colorless. When diluted to 1,000 cc. and allowed to stand for three to four weeks, the solution gives only a slight blue coloration with $K_4Fe(CN)_6$. If a normal chromic sulphate is dissolved and diluted to the same degree, only a slight turbidity is observed, but very little, if any, precipitate separates out after 24 hours' standing and the solution remains light green. This comparison shows in a qualitative way that the chromic salt in solution is very much less susceptible of hydrolysis and decomposition with dilution.

Next, a mixture of a basic ferric sulphate and basic chromic sulphate solution was quantitatively studied. This solution is prepared by placing 50 g. of ferrous sulphate crystals in 50 cc. of distilled water containing 17.4 g. C. P., 1.84 H_2SO_4 and then gradually introducing 9 g. of sodium dichromate crystals, $Na_2Cr_2O_7.2H_2O$ to the mixture. Upon introduction of the sodium dichromate, ferrous sulphate crystals are dissolved, much heat is given off, and a thick dark liquid containing a mixture of the basic ferric sulphate and chromic sulphate in solution is obtained. This solution appears black by reflected light and dark red by transmitted light. It has a specific gravity of 1.46. Analysis shows that it contains, per 10 cc.—

0.07312 equivalents of $SO_4^=$ (from acidity determination).
0.06820 equivalents of Fe^{+++}.
0.02117 equivalents of Cr^{+++}.

The ratio of the number of equivalents of the sulphate radical $SO_4^=$ (which is divalent) to that of Fe and Cr combined (each of which is trivalent) is 0.819 : 1.000, so that there are not enough sulphate radicals to go with iron and chromium in the solution. This condition may be summarized in the formula:

Radical.....M^{III} : $SO_4^=$: (OH^-) $(M^{III} = Fe^{+++} + Cr^{+++})$
Ratio of equiv. 1.000: 0.819 : 0.181 (by difference).

The idea of using such a quantity of H_2SO_4 and making a liquor

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as concentrated as this needs some explanation. In the first place, if a liquor is to be placed on the market it has to be in as concentrated a form as practicable in order to save freight charge in transportation and to avoid inconvenience in handling. In the second place, a tanning liquor must always contain some degree of basicity. Too much acid left in the liquor not only means just so much alkali needed for neutralization before the tanning operation, but also involves a danger of not getting the proper degree of basicity for tanning in the hands of men who are not quite familiar with chemistry. We find by a number of experiments that this proportion of the sulphuric acid represents the minimum quantity that should be present in order to make the liquor alkaline enough to be used for tanning without neutralization (Chrome-Iron Joint Tannage) and yet acid enough to make the liquor keep for a considerable period without danger of precipitation.

A quantity of this concentrated liquor measured through a burette is diluted to different volumes with distilled water, and the solution allowed to stand for 24—48 hours. The supernatant liquid is filtered and pipetted for analysis. Chromium is determined by Na_2O_2 oxidation and by titration against sodium thiosulphate solution using KI and starch as indicator. Ferric hydroxide that is precipitated by Na_2O_2 in the same sample is filtered off,* washed and dissolved from the filter with hot dilute HCl solution. The amount of iron in this solution is determined by the Zimmermann-Reinhardt method. These results are tabulated as follows:

* When much iron is present, a considerable amount of the chromate is absorbed by the ferric hydroxide precipitated from the peroxide oxidation, so that the result of the chromium determination in the filtrate is always too low while the iron by the Zimmermann-Reinhardt method becomes high. To avoid this error, the supernatant chromate solution after the peroxide oxidation is decanted through a filter and the ferric hydroxide left in the beaker is dissolved by adding a small amount of hot dilute HCl. The solution is now diluted and the ferric hydroxide re-precipitated with an alkali at a boiling temperature. A small amount of Na_2O_2 may be introduced with the alkali, in which case care must be taken to decompose all the peroxide again. If a large quantity of chromium is also present, a second re-precipitation is necessary in order to remove all the chromium from the ferric hydroxide.

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Hydrolysis and Decomposition of a Mixture of Ferric Sulphate and Chromic Sulphate in Solution Compared.

Sample	No. of times of dilution	Color of solution after dilution	Character of solution after 2 days standing	Cc. supernatant solution taken for analysis	Cc. $KMnO_4$ sol. consumed N = 0.1139 (for iron)	Cc. $Na_2S_2O_3$ consumed N = 0.04843 (for Cr)	Mg. $Fe_2(SO_4)_3$ in sol. as Fe_2O_3 corr. to 0.2 cc. orig. sol.	Mg. $Cr_2(SO_4)_3$ in sol. as Cr_2O_3 corr. to 0.2 cc. orig. sol.	Ratio of Fe_2O_3 to Cr_2O_3 in solution
Orig. conc. solution	No dilution	(Original solution black)	Remains a clear, black solution	(10 cc. conc. liquid dilu. to to 100 cc. and immediately 5 cc. taken)	9.98	21.87	36.4	10.7	3.40
10 cc. conc. solution dil. to 100 cc.	10	Solution black by refl. light, dark red by trans. light	Black solution, but ppt. at bottom noticeable	5 (Corr. to ½ cc. orig. sol.)	9.83	21.85	35.8	10.7	3.34
5 cc. conc. solution dil. to 250 cc.	50	Solution dark red. Turbidity after 30 min.	Dark red supernatant solution with yellow ppt. at bottom	10 (Corr. to 0.2 cc. orig. sol.)	3.84	8.71	34.9	10.7	3.26
2 cc. conc. solution dil. to 500 cc.	250	Solution brown Turbidity after 5 min.	Greenish-brown supernatant solution with yellow ppt. at bottom	50 (Corr. to 0.2 cc. orig. sol.)	2.88	8.66	26.2	10.6	2.47
1 cc. conc. solution dil. to 1000 cc.	1000	Solution dull yellow. Turbidity after 3-4 min.	Light green supernatant solution with much yellow ppt. at bottom	200 (Corr. to 0.2 cc. orig. sol.)	1.69	8.55	15.4	10.5	1.47

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It is evident that the extent of hydrolysis increases with dilution.

$$\begin{array}{ccc} Fe_2(SO_4)_3 \rightleftharpoons 2Fe^{+++} & + & 3SO_4^{=} \\ + & & + \\ 6H_2O \rightleftharpoons 6OH & + & 6H^{+} \\ \Updownarrow & & \Updownarrow \\ 2Fe(OH)_3 & & 3H_2SO_4 \\ \Updownarrow & & \\ Fe_2O_3.xH_2O & & \end{array}$$

(yellow crystalline ppt. of dehydrated ferric hydroxide).

This is strictly according to the Mass Action principle, for a greater dilution means a greater active mass of water and hence the following reaction is pushed to the right:

$$Fe_2(SO_4)_3 + 6H_2O \rightleftharpoons 2Fe(OH)_3 + 3H_2SO_4.$$

Another way of interpreting this is that with greater dilution the hydrogen ion concentration is correspondingly lowered. That is to say, the alkalinity of the solution is increased and consequently the degree of hydrolysis is increased.

The above results show how ferric sulphate in solution is more readily hydrolyzed and decomposed than the chromic sulphate. To show this more clearly the following curves are plotted:

Fig. – 1

Curves Showing $Fe_2(SO_4)_3$ and $Cr_2(SO_4)_3$ Remaining in Solution vs. Dilution

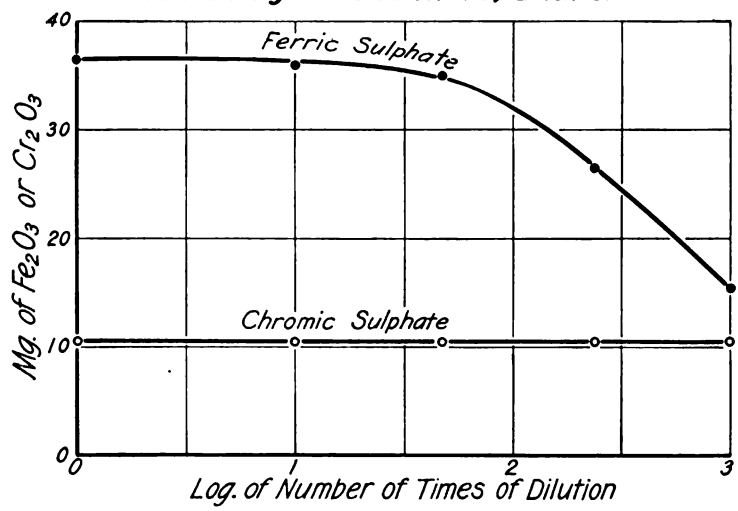

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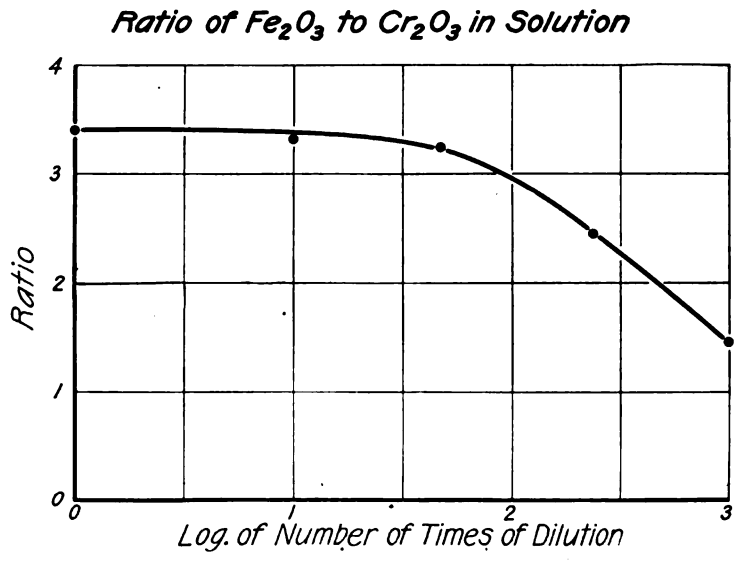
FIG.-II



The precision of the above determinations is not better than ½—1 per cent. For, when the precipitate, especially in the last two solutions, separates out abundantly in a fluffy manner and only the supernatant clear liquid is taken for analysis, the original volume ratio does not exactly hold, but the error is small and can be neglected.

A mixture of the corresponding chlorides, namely the ferric chloride and the chromic chloride, was taken and similarly studied. The basicity relation as determined by analysis was as follows:

Radical..... M^{III} : Cl^- : OH^- ($M^{III} = Fe^{+++} + Cr^{+++}$)

Ratio of equiv. 1.100: 0.800 : 0.200 (by difference).

Dilution in much the same way as in the corresponding sulphate mixture was carried out. In no case was there any precipitate observed, not even where the original solution of the mixture was diluted to 2,000 times, the original solution having a concentration of 34.52 g. iron as Fe_2O_3 and 20.00 g. chromium as Cr_2O_3 per liter. This shows remarkably that ferric chloride is far more stable toward dilution than is ferric sulphate for the same basicity, and in this respect ferric chloride behaves in much the same way as chromic chloride or other chromic salts. The con-

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clusion to be drawn from this would be that in order to get a stable liquor as much of the ferric salt in the tan liquor as possible should be in the form of a chloride, but unfortunately the main supply of ferrous salt is already in the form of a sulphate ("copperas") owing to the cheapness and convenience of sulphuric acid for pickling purposes in the foundry and steel works. With the chlorine oxidation, however, a third of the acid radical is conveniently secured in the form of a chloride.

[*To be continued*]

IMPROVED FORMULAE FOR THE CALCULATION OF INORGANIC IMPURITIES IN SULPHATED OILS

By Ralph Hart.

Rec'd. February 2 1921.

In a recent number of this JOURNAL[1] it was shown that inorganic impurities in sulphated oils may be determined indirectly by means of the following formula:

Inorganic Impurities =

$$\text{Ash} - [0.0634(2A + As) + 0.0473(2A - As)] \qquad (1)$$

where As represents organically combined SO_3 expressed in mg. KOH per gram and A, fixed alkalinity expressed in the same terms.

It was also stated that the second term on the right represented Na_2SO_4 due to ashing the combined SO_3 and that the third term represented Na_2CO_3 in the ash due to the ignition of sodium soaps in the oil.

In applying the above formula, the carbonate term must always be positive, negative values being disregarded. In the sulphate term, 2A must be equal or less than As; if greater, 2A is replaced by As.

In its present form, this formula is somewhat confusing in its application. It was found, however, that it may readily be simplified, namely, as follows:

Case I.—When 2A is equal or less than As, it is evident that there can be no carbonate in the ash and therefore the carbonate term equals zero. Hence, the above formula is reduced to the following:

$$\text{Inorganic Impurities} = \text{Ash} - 0.0634\ (2A + As) \qquad (2)$$

[1] This JOUR., 15, 404 (1920).

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Case II.—When 2A is greater than As, Na_2CO_3 will be found in the ash and the carbonate term must be retained. In this case however, we must substitute As for 2A in the sulphate term. Making this change in equation (1) and simplifying, the following is obtained:

Inorganic Impurities = Ash — (0.0795As + 0.0946A) (3)

Formulae two and three may be more conveniently stated by substituting per cent. combined SO_3 for its equivalent As. Let S equal per cent. combined SO_3, then $As = \frac{112}{80} \times 10\ S = 14\ S$.

Making this substitution we obtain the following:

Case I.—When A is equal or less than 7 S (*i. e.*, in the absence of carbonate)—

Inorganic Impurities = Ash — 0.1268 (7 S + A) (4)

Case II.—When A is greater than 7 S (*i. e.*, in the presence of carbonate)—

Inorganic Impurities = Ash — 0.0946 (11.77 S + A) (5)

Data required: Ash, combined SO_3 (S), and fixed alkalinity (A) in mg. KOH.

The following table is taken from the paper cited above, including, however, only the data required for calculating salts and impurities by the last two formulae:

	No. 3. Per cent.	No. 4. Per cent.	No. 7. Per cent.	No. 10 Per cent.	No. 13 Per cent.
Combined SO_3 (S)	1.95	1.91	1.93	2.65	2.00
Fixed alkalinity (A) mgms. KOH	3.70	9.40	24.5	5.80	4.52
Ash	3.05	4.46	5.14	6.01	2.51
Salts found, old method	0.74	1.51	0.71	2.79	0.16
Inorganic impurities, new method	0.85	1.57	0.67	2.92	0.16
Difference	—0.11	—0.06	+0.04	—0.13	0.00

The average difference is —0.05. All but No. 7 were calculated by Formula (4), the latter by Formula (5).

In a recent article published by Dr. C. G. Bumcke,[2] he showed that the direct method for determining organically combined SO_3 by decomposition and titration may be made very accurate by the simple expedient of doubling the concentration of the acid that was originally specified by the present writer when the method was first proposed. Consequently, should this method displace the old gravimetric method for combined SO_3, there would be

[2] This Jour., 16, 7 (1921).

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little need for the determination of SO_3 as salts. On the other hand, it would be more desirable to determine the inorganic impurities which by the present methods are only partically estimated, for example, by analyzing for SO_3 as salts. Formulae (4) and (5) above offer a simple means of calculating total inorganic impurities from data usually determined for the other tests.

New York, N. Y.

ABSTRACTS.

The Care of Leather. By F. P. VEITCH, H. P. HOLMAN and R. W. FREY, *Farmers' Bulletin 1183,* U. S. Dept. of Agriculture. A brief treatise containing suggestions for a judicious selection of boots and shoes, harness, belts, and bookbinding and bag leathers and tells how to care for them in order to obtain the maximum service.

Laboratory Wearing Test to Determine the Relative Wear Resistance of Sole Leather at Different Depths Throughout the Thickness of a Hide. By R. W. HART, *Technologic Paper 166,* Bureau of Standards. Test pieces were obtained at four different layers of the leather, the grain surface, a depth of one-third the thickness of the leather, a depth of two-thirds the thickness, and the flesh surface. From data obtained it appears that the interior portions have a greater resistance to wear than either the grain or the flesh sides. The grain membrane has very little resistance, the grain side has a slightly greater resistance than the flesh side. There is no specific surface which has the greatest wear resistance.

Hides and Leather in France. By NORMAN HERTZ, *Special Agents Series No. 200,* U. S. Dept. of Commerce. A thorough report and detailed discussion of the local supply of hides and skins, the domestic production of leather and leather goods in France, the foreign trade in such merchandise, the special requirements of the various leather-using industries, and the most advantageous methods to be pursued by American tanners in selling their products to the French.

Raw Materials for Tanning in the Belgian Kongo. By S. H. CROSS, *Commerce Reports,* Feb. 7, 1921. Owing to the increased Belgian demand for tanning materials an investigation of the applicability of the raw materials of the Belgian Kongo has been instituted. In this colony there are numerous native trees with barks rich in tannin. Among these is the "Mwena," a species of mangrove abounding on the banks of the Lower Kongo and its tributaries, the bark of which contains a minimum of 15 per cent. of tannin, the trunk and roots producing an extract of 50 to 55 per cent. tannin. Several varieties of the *Terminalia* give barks which yield a dry extract of 62 per cent. tannin, entirely soluble in the cold. This

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extract is said to produce an extremely light and well tanned leather. It is considered that the tan-bark industry is one of great potential importance for the Kongo.

Differentiation of Extract of Old Fustic (Morine) and Quercitron Extract (Quercetrin). By E. JUSTIN-MUELLER, *Bull. Soc. Chim.*, **27**, 844 (1920). These two extracts appear quite different under the microscope, that of quercitron showing more or less agglomerated granules, while that of old fustic shows well-defined crystals. If a trace of either extract (dry or concentrated liquid) is dissolved in sulphuric acid (66° B., sp. gr. 1.84) and then diluted with water, the extract of old fustic remains bright orange-yellow, while that of quercitron is decolorized. *J. S. C. I.*

Theory of the Tanning (Hardening) Process in Dilute Gelatine Gels with Formaldehyde. By L. REINER, *Kolloid Zeits.*, **27**, 195 (1920). Two to 3 per cent. solutions of formaldehyde harden 5 per cent. gelatine solutions in a few minutes, whilst a 1 per cent. solution of formaldehyde requires several days. Hardened gelatine softens at elevated temperatures, the temperature of softening being dependent on the amount of hardening and the concentration of the gelatine, but higher than the melting point of the untreated material. The softening of the hardened gelatine commences at the centre of the mass and spreads throughout the whole, and on raising the temperature sufficiently the mass becomes liquid. If the softening temperatur is above 90° C., complete liquefaction is no longer possible. The hardening takes place more readily on the surface and at the walls of the containing vessel. On cooling a melted hardened gelatine it solidifies at a temperature below the solidification point of the untreated material. The hardening process is reversible, for on heating hardened gelatine with a little water at 100° C., formaldehyde is evolved and the gelatine regains its original physical properties. The hardening process may be stopped and reversed by the addition of small quantities of ammonia. *J. S. C. I.*

The Miles-Acid Process on Tannery Waste. By E. S. DORR, *Public Works*, **49**, 403 (1920). In June, 1916, a sample of tannery waste was submitted to the Miles-acid process. The sample was very high-colored and was heavily charged with organic and mineral matter, 6,449 parts per million, of which 4,886 were mineral and 1,583 organic and volatile. Upon the application of sulphur dioxide the waste cleared in about five minutes and was well settled in half an hour. The dark blackish-red color was bleached to straw color, the SO_2 used was at the rate of 860 parts per million (7,167 lbs. per mg.). Probably 900 parts per million (7,500 lbs. per mg.) would be advisable to secure sterility. Bacterial reduction was not noted. The odor was completely killed. The reduction in the organic and volatile matter, including suspended solids, was 50 per cent.

The precipitated sludge was at the rate of about 4 tons (dry) per million gallons with a grease content of 16.88 per cent. and ammonia con-

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tent of 7.50 per cent. in the undegreased and 9 per cent. in the degreased sludge. In pounds the amounts are 6,640 lbs. degreased sludge, or fertilizer material, and 1,360 lbs. grease.

The fertilizer with 9 per cent. ammonia at $7.50 per unit (value of tannery tankage in August, 1920) would be worth $67.50 per ton, or 3.3 tons would be $222.75 per million gallons.

The grease at the prices assumed in the New Haven investigation (and tannery grease is probably worth more) would be worth, at 5 cents per pound, $68 and at 8 cents per pound $108.80 per million gallons. So that the total value of grease and fertilizer would run from $290.75 to $331.55 per million gallons treated, according to the quality of the grease. (The free fatty acids were 48 per cent., percentage of unsaponifiable was not determined.)

On the other hand, the cost of operation would be high. About five times as much acid would be required, and twenty times as much sludge per million gallons would have to be handled, as at the Boulevard sewer in New Haven. The cost of operation at that outlet was reckoned at $20.98 per million gallons, of which $10.74 was for acidification, as the flow was not large, about 6,000,000 gallons per day. The New Haven figures may be taken as a basis for estimating the probable cost of handling tannery waste. Correcting, in the ratios indicated above, for the heavier tannery waste, the cost per million gallons would be $161.22.

The values of the products have been figured above at from $291 to $331 per million gallons treated. The estimate therefore shows a surplus of values over costs of $130 to $170 per million gallons.

In view of the fact that, so far as the writer is aware, no revenue has been obtained from tannery wastes, but, on the contrary, they are a source of expense for disposal, it would seem that this process is worthy of the attention of tanners. In addition, the facts that the sludge and effluent are inodorous, that the color is so bleached that with reasonable dilution it would not be noticeable except close to the outlet, and that the effluent is sterile or can be made so by the addition of acid (for the cost of which there is ample margin between values and costs) should still further commend it to attention and experiment.

The Proteolytic Factor in Tannin Analysis. By W. MOELLER, *Collegium*, **603**, 307-19; **604**, 374-81. The error in the non-tannin determination due to the presence of hydrolyzed hide substance in the non-tannin residue cannot be corrected by making a blank determination with water, for the hydrolyzed hide substance in the non-tannin residue is greater than in the blank. In a blank determination with unchromed hide powder 0.01053 gram of hide substance (calculated from the per cent. nitrogen) was found in the non-tannin residue and in a blank with chromed hide powder 0.003807 gram of hide substance was found by the shake method and 0.003752 gram by the filter method. Analysis of about fifty tanning materials are given in which the dissolved hide substance in the non-tannin residue was determined. The amount of hide substance, after subtracting

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the blank, was positive in all but three cases and usually amounted to several per cent. of the non-tannin residue, the highest per cent. being 11.14. This introduced a maximum error of 0.8 per cent. in the percentage of non-tannin if the blank was subtracted and an error of 3.1 per cent. if the blank was not used. Nitrogen determinations on six tanning materials gave values varying from 0.015 per cent. for tannin to 0.15 per cent. for oak wood, corresponding to 0.06 and 0.83 per cent. respectively of hide substance. This nitrogen may be present either in plant proteins and alkaloids or in nitrates and nitrites, and since the former are retained by the hide substance and the latter are present in very small amounts, this nitrogen does not affect the values given for the amount of nitrogen in the non-tannin residue. Chroming the hide powder was introduced because chroming reduces hydrolysis by water and gives a much lower blank. However, when an analysis was made of several tanning materials by the shake method, using unchromed hide powder in one case and chromed in the other case, a much greater non-tannin residue was found with the chromed hide powder, although the amount of dissolved hide substance was about equal in the two cases. While therefore chroming prevents hydrolysis by water alone, it does not prevent hydrolysis by the substances present in the non-tannin solution, such as organic non-tannins, or acids, bases and salts. Shaking also may increase the hydrolysis and may mechanically break up the hide powder so that it will pass into the non-tannin solution. The ideal solution of the difficulty would be to use a material which cannot hydrolyze, but if this cannot be found, it will be necessary to prevent hydrolysis by some method such as a stronger preliminary tanning with plant or mineral tannin. Investigations, in several directions, were carried out, but no suitable method for preventing hydrolysis has yet been found. The view that the hide powder method gives results which agree closely with the results obtained in actual tanning, is false for the behavior of hide powder is different from that of unhaired skins and also the concentration of the tannin is quite different in the two cases. In tanning the tannin can always be considered to be present in excess while in the analysis there is a great excess of hide powder and therefore hydrolysis occurs in the latter but not in the former case. I. D. C.

The Determination and Retention of Free Sulphuric Acid in Leather and Hide. By C. IMMERHEISER, *Collegium*, **604**, 360-7 (1920). In reply to Moeller's criticism (*Coll.*, **588**, p. 111) of his method for determining free sulphuric acid in leather (*Coll.*, 1918, p. 581), Immerheiser gives the results of two experiments in which he added a definite amount of sulphuric acid to leather and found that the acid was all extracted by water even if present in rather large amounts. While the presence of chlorides will cause a loss of sulphuric acid by this method, the analysis of several materials, including mangrove, showed that the amount present was too small to affect the results appreciably. Neither was there a loss of acid, by oxidation of organic matter, during the analysis of a mixture of acid,

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sand and dry extract of leather. No increase was found in the acid content of leather tanned with Neradol D or ND, after storage for three years, indicating that acid is not formed by oxidation of these tanning materials. The sulphuric acid neutralized by hide is not only bound to the mineral matter but also to organic constituents of the hide, especially those containing nitrogen. The water extract of leather which had been treated and partially decomposed by sulphuric acid, was unusually rich in nitrogen, the nitrogen content in a few cases reaching ten times the normal amount. In order to determine how much acid was neutralized by hide and leather and the effect of tanning on this neutralization, titrations were made of unhaired raw hide, limed hide, of hide tanned with oakwood extract for 5 hours, 24 hours, 90 hours and 9 days respectively and of leathers tanned with various materials. In the preliminary trials the titration was made directly on the moist, powdered hide or leather, using congo red paper as the indicator. For more exact results the material was treated with an excess of acid, filtered and the amount of acid in the filtrate determined. The author concludes that there is a strong tendency for hide and leather to react with free sulphuric acid; that the ability of leather to react with acid is much less than that of hide, and is proportionately less the greater the acidity of the tannin; that free sulphuric acid cannot ordinarily be present in leather; and that it is necessary, in testing leather for harmful ingredients, to determine the nitrogen in the water extract in order to determine whether there has been a decomposition due to acid.

I. D. C.

The Influence of the Composition of Water in its Use for Tanning Purposes. By G. GRASSER, *Häute und Lederber.*, No. 22 (1920), through *Ledertechn. Rund.*, **12**, 127 (1920). According to Eitner, soft water makes hides thin and flat while hard water fixes the dirt and grease in the hide. Calcium and magnesium sulphate, in general, produce good swelling, while calcium and magnesium carbonate are detrimental. Water that contains much carbonate is, therefore, best neutralized with sulphuric acid. Calcium sulphate makes dyeing difficult and gives the leather a coarse feel. Whether the use of hard water for the extraction of tanning material is detrimental, or causes a loss of tannin, remains an open question. Chlorides arrest the swelling of hide, makes tanning difficult and when present in leather in large amounts attracts moisture. The use of water in the tannery which contains such bacteria as decompose protein, especially putrefactive bacteria which attack the corium and liquefy hide substance, is dangerous. Putrid water causes dull grain as well as decomposition of the hide. There are many effective chemical process for softening water. Simply boiling the water may reduce the hardness about one-half and at the same time almost completely kill the dangerous germs. When such treatment is not practicable, it can be sterilized with ozone, or by the addition of 0.2 per cent. acetic or sulphuric acid the number of injurious germs can be reduced.

G. W. S.

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Researches on the Processes of Tanning—I. By W. MOELLER, *Leder-techn. Rund.*, **12**, 89, 97, 108 and 116 (1920). An investigation of the adsorption process with particular reference to the absorption of tannin by hide from solutions of varying concentrations for different periods of time. The experiments were made with phenol, tannic acid and sulphited quebracho extract using solutions of approximately 1, 3½ and 6 per cent. strengths. The amount absorbed was calculated by difference after measuring the concentration of the external solution. The results with phenol solutions show that the absorption of phenol by hide powder follows the adsorption law and that equilibrium is not attained until after 30 days. For the tannic acid solutions for periods of action of 1 and 8 days it is apparent that the adsorption law is not valid since the hide powder absorbs more in the mean concentration than in the highest concentration. Equilibrium is practically attained with the dilute solution in 24 hours, since the tannin is almost quantitatively removed in this time; in the 3.5 per cent. solution after one month; and in the 6 per cent. solution only after three months. When equilibrium is attained the adsorption law apparently is valid. The quebracho solutions did not show the anomaly exhibited by the tannin solution of mean concentration. Its adsorption was regular although equilibrium was not obtained until after longer periods of action. Thus the tannin is not removed from the dilute solution (1 per cent. of solids) until after a period of 2 months, while it was not obtained with the stronger solutions for periods up to 3 months. Experiments made with quebracho solutions, starting with 1 per cent. solutions and strengthening periodically, showed that the greatest amount absorbed by the hide powder (about 90 per cent. of its dry weight) was removed after 80 days and after 120 days there was a slight decrease in the amount absorbed.

Von Schroeder and Paessler (*Gerberei-Chemie*, Berlin, 1898, p. 397) conducted similar experiments with hide and tannic acid, but did not consider the time factor. They arrived at the conclusion that with increasing concentration of tannin in liquors there is an increase in the amount of tannin adsorbed by the hide up to a maximum, then a decrease to a minimum when further increase in concentration of the liquor causes no change. They explained the fact the hide absorbed less from the stronger solutions by the assumption that tanning with the stronger solutions was only superficial and that the surface of the hide particles was completely tanned so as to form a protective coating which prevented further penetration of the tannin. This view the author considers the most likely, but it is incomplete and needs elaboration in view of the results obtained by extending the time period. The author elaborates the assumption of von Schroeder and Paessler with the aid of his peptization theory. The protective coating of tannin which is precipitated around the fibers when tanning with a strong solution is again peptized in the course of time and further penetration of the tannin solution is again permitted. The fact that such a coating obtained with the strong solution is due to a difference in degree of dispersion of the tannin particles. In

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the lesser concentrations the tannin particles are very fine and the tanned part of the hide remains permeable while in the highest concentration the opposite is the case. G. W. S.

The Chemical Action of the Sulphonic Group Artificial Tannins. By W. MOELLER, *Ledertechn. Rund.*, **12**, 154 and 161 (1920). The tannins are defined as "substances which, alone or in contact with pelt, form colloïdal solutions and which prevent hydrolytic and fermentative decomposition of the hide by being adsorbed in irreversible form." The synthetic tannins of the sulphonic group augment the hydrolysis of hide substance and therefore are directly opposed to the true tannins. It was first believed that the increased amount of hide going into solution with the use of synthetic tannins was due to the presence of free sulphuric acid in these extracts. but as the result of the experiments given in this paper the author declares that the increase is due to hydrolysis of the hide substance by the free sulphonic acids contained in them. In their ability to hydrolyze hide substance and thereby render it soluble the synthetic tannins are placed midway between sulphuric acid which has the least effect and pure β-naphthalene sulphonic acid which has the greatest.

The method used for determining the amount of hide substance hydrolyzed consisted of adding 5 grams of air dry hide powder to 100 cc. of solutions of the different substances of varying concentration and shaking just sufficiently to get a good mixing. These mixtures were allowed to stand for different periods of time after which the solutions were filtered off and the nitrogen determined in an aliquot of the filtrate. It is claimed that hide powder treated with water in this manner gives a percentage of soluble hide substance that is constant which is due to the weakly hydrolyzed condition of the hide powder used. Ordoval C, ordoval 2G, neradol D and ND were tested and it was found that the amount of hide substance rendered soluble increased with increase in concentration and, in general, with increase in the period of contact. In the case of neradol ND with a solution containing 10 per cent. of tannin, after 28 days 58.5 per cent. soluble hide substance was found. When these extracts were mixed with 50 per cent. of solid quebracho extract, the amount of hide substance rendered soluble was reduced, but it still remained considerably more than would be obtained by a solution of a true tanning material. Where pure water dissolved 0.65 per cent. hide substance a N/1 solution of sulphuric acid dissolved 6.56 per cent. in a nine-day period and a N/1 solution of β-naphthalene sulphonic acid dissolved 83.44 per cent. The author considers that the so-called synthetic tannins are mixtures, a part of which consists of an actual tanning substance and a part of free sulphonic acids which, in their action on hide are directly opposed to tanning substances. The free sulphonic acids in the artificial tanning material first splits the micellar bonds of the hide fibrils. The second step is further decomposition of the micells into the protein molecule. The last phase is the destruction of the protein molecule. The sulphonic acids joining with the cleavage products or their free amino acids to form water soluble

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products. It is claimed that the cause of detrimental properties of leather produced with the use of artificial tanning materials is not, as erroneously thought, due to the free sulphuric acid, but to the much stronger action of the sulphonic acids. G. W. S.

PATENTS.

Synthetic Tanning Agents. British Patent 148,898. CHEMISCHE FABRIKEN WORMS AKT.-GES., Frankfurt-on-Main, Germany. July 10, 1920. Synthetic tanning agents are obtained (1) by coupling by means of appropriate atoms or groups aromatic hydroxy compounds or their metal salts with aliphatic hydroxy compounds; (2) by similarly coupling aromatic compounds free from hydroxy groups with aliphatic hydroxy compounds; (3) by repeated coupling of aromatic compounds by means of aldehydes, phosphorus pentoxide, etc., to obtain products of high molecular weight and introducing acid groups to solubilize them. According to examples:—phenol is sulphonated by sulphuric acid, glycerine is added, and the mixture condensed with formaldehyde; napthol sulphonic acid and glucose are heated with formaldehyde; cresol sulphonic acid is heated with glucose and formaldehyde; cresol sulphonic acid is heated with glucose and sulphur chloride; sodium 1-naphthylamine-5-sulphonate is heated with glucose and formaldehyde; naphthalene sulphonic acid is heated with glucose and formaldehyde; coal-tar phenols of boiling-point 185°-200° C. are heated with sodium sulphite and formaldehyde and the resulting tanning agent is heated with glucose and formaldehyde; the same phenols are heated with sodium sulphite, formaldehyde, and sulphite-cellulose; *p*-dioxydiphenylmethane is sulphonated by sulphuric acid and the product heated with formaldehyde; *p*-dioxydiphenyl is condensed with cresol sulphonic acid and formaldehyde, and the neutralized product is heated with sodium sulphite; *p*-dioxysulphobenzide is sulphonated by sulphuric acid and the neutralized product is condensed with sodium phenol sulphonate and formaldehyde; *p*-dioxydiphenylmethane is sulphonated by sulphuric acid and the product heated with 1-naphthylamine-5-sulphonic acid and phosphorus pentoxide; naphthalene sulphonic acid is heated with sulphuric acid and formaldehyde and the resulting tanning agent is heated with cresol sulphonic acid and formaldehyde. Specification 18258/13 is referred to. It is also stated that in the process described in Specification 148,897 glycerine, waste sulphite-cellulose lye, etc., may be coupled with vegetable tannins. The products may be used alone or mixed with other tanning agents, or in combined tanning processes wherein both vegetable and mineral tanning agents are used.

Wetting-Out Machine for Leather. U. S. Patent 1,357,021. E. B. AYRES and T. H. RHOADS, Philadelphia, Pa. Filed Mar. 26, 1920.

Bark-Peeling Machine. U. S. Patent 1,358,993. W. S. SHAW, Chicago, Ill. Filed Jan. 30, 1920.

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CORRECTION.

Under the proposed changes in by-laws published in the March number, page 108, section 7(b) should read as follows:

By special arrangement with the Society of Leather Trades Chemists, terminable at will at the end of any calendar year by either party to the arrangement upon three months notice, any member, etc., etc.

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ANNUAL MEETING.

The eighteenth annual meeting of the A. L. C. A. will be held at the Hotel Ambassador, Atlantic City, N. J., on June 9, 10 and 11, 1921.

The following schedule of rates has been received:

European plan, per day:

Single	$6, $8, $11
Double	$8, $10, $13
Triple	$10, $12, $15

American plan, $6 per person a day in addition to above rates.

Reservations should be made by communicating direct with the management of the Ambassador.

NOTICE.

Members who desire German technical books may obtain the same by applying to Ing. Josef Jettmar, Praha-Vinohrady 1495, Republic of Czechoslovakia, who has kindly extended his services to his colleagues in the matter of procuring such books as may be desired and will also consider exchanges for English books.

Ing. Jettmar also advises that he can send two copies of his book, Die Eisengerbung (see page 93) to the U. S. A., charges paid, for one dollar ($1).

BOUND VOLUMES.

Bound volumes of the JOURNAL for 1920 are now ready for distribution by the Secretary. Unbound copies to be exchanged for bound volumes should be sent to the Secretary, 22 East 16th St., New York, N. Y., and should be in good condition. The cost of exchange will be $2.10 delivered.

THE AMERICAN OIL CHEMISTS ORGANIZED.

For a number of years the leading chemists in the cottonseed oil industry have been fraternally associated in the Society of Cotton Products Analysts. This organization primarily concerned itself with perfecting methods of analysis used in the cottonseed crushing and refining industry. It did for the edible oil trade what the Association of Official Agricultural Chemists does for

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the food industry; the Society for Testing Materials for the paint trade; and the Leather Chemists' Association for the leather and tanning industry. Certain specific qualifications as to membership limited it in numbers to those highly specialized, but insured a large amount of important investigational work. The great war drew this country into a large international trade in several of the vegetable oils which became keen competitors of cotton oil. This caused a commensurate widening of the Society's interest with the result that at the annual meeting of the Society in May, 1920, it was reorganized under the name of the American Oil Chemists' Society. Its aim can no better be expressed than in the words of Article II of its constitution:

Section I. The object and purpose of the Society shall be, first to unite for fraternal and business purposes all chemists interested in the promotion of the chemistry of Fats, Oils, Waxes, and Allied Industries.

Section II. To cultivate the ties of friendship that should exist between those who have adopted a similar profession and who enjoy common interests.

Section III. To encourage the writing of original papers on subjects pertaining to chemical work, to foster and encourage chemical research, to promote a spirit of cooperation and interchange of ideas and to strive for the adoption of uniform methods of analysis to be used by all the members of the Society.

Section IV. To exert our influence and efforts towards securing the enactment of State Laws safeguarding and protecting the practice and dignity of the chemical profession.

Section V. To place the profession on the high plane its dignity deserves, and to secure for those engaged in it adequate recognition of their services, in keeping with the years of study required to master it, and the high character of those to whom only its responsibilities should be entrusted.

All persons engaged in chemical work relating to fats, oils, waxes and allied interests are eligible for active membership provided they have had at least five years chemical training. Its meetings are held once a year, usually in May and in conjunction with the Interstate Cottonseed Crushers' Association. It regularly publishes its transactions and maintains the Chemists' Section in *The Cotton Oil Press*, a journal devoted exclusively to the interests of the edible vegetable oil industry.

Its membership, however, is not limited to chemists and technologists engaged exclusively in the edible oil trade, but includes

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also those interests in its so-called industrial or technical aspects. Although the entire vegetable oil industry is founded upon more or less similar practice in obtaining the oil, the unified character of the industry ceases at that point and then splits up into several rather well defined branches, namely those of edible oil, paint, soap, vulcanization, sulphonation, etc. The oil industry is too elastic to permit any oil to be pocketed; therefore, no oil chemist should confine his interest exclusively to his given line. Since most of the oils dealt with are industrially more or less interchangeable, their chemical control and technological development can only be properly fostered by sympathetic and intimate contacts between science and industry. Such are furnished by the American Oil Chemists' Society.

Any one interested in the activities of this new organization may obtain further information from Mr. Thos. B. Caldwell, Sec. and Treas., Wilmington, N. C.

THE QUEBRACHO FORESTS OF SOUTH AMERICA.

Personal Notes and Observations in Argentina and Paraguay.

By Geoage A. Kerr.

Rec'd. March 9, 1921.

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It is a somewhat remarkable caprice by which nature has ordained that the present principal sources of the two most important vegetable tanning materials—quebracho and chestnut—should be situated in the two continents of the western hemisphere, and at the same time, that they should be analogous in so many respects, that anyone with a knowledge of the habitat of the one, may glean a very good idea of the habitat of the other from what is to follow. For instance in range of latitude and width of forested area, distribution, distance from the sea coast, and in many other points they have much in common.

In Argentina and Paraguay, there are three varieties of quebracho tree, so-called, *viz:* in the order of their importance, the quebracho *colorado* or red quebracho, quebracho *blanco* or white quebracho, and the quebracho *macho,* which may mean either the male or strong quebracho, most probably the latter, but the author has never met anyone who could enlighten him as to this.

It is the first of these varieties with which we are concerned here, as it not only vastly outranks the others in quantity, but

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also in general importance, as being the raw material of the tanning extract of commerce, and of immense value and utility as timber. The quebracho *blanco* has value only as timber, while the quebracho *macho* is not sufficiently plentiful to be of much importance in any respect, although it ranks next to quebracho *colorado* of the more northern latitudes in tannin content. The only considerable quantities of this class of quebracho coming to the writer's notice, is in northern Paraguay, and for the most part east of the river Paraguay. In Argentina, if existant at all—in the course of travel through hundreds of leagues of forested country none was seen by the author—it is not generally used for the production of tanning extract, but it is sometimes used in conjunction with quebracho *colorado* in some of the extract plants of alto Paraguay, this however is only possible when the price of extract is high enough to offset the difference in yield, which is 15 per cent. to 20 per cent. lower.

Quebracho *colorado* is found in quantity from lat. 20° S. to lat. 31° S., the length of the belt being approximately eleven degrees or 760 miles and beginning at the northern limits of Paraguay it extends south to about one-third way through the Argentine province of Sante Fe, the distance being equivalent to that from northern Pennsylvania to the southern limit of the North American chestnut belt in Alabama. This region embraces the Chaco Paraguayo, the Argentine province of Formosa lying between the rivers Pilcomayo and Bermejo, the territory of the Argentine Chaco, the province of Sante Fe and that of Santiago del Estero. There is also some quebracho in the southeastern portion of the province of Tucuman, but the total forested area of this province being only some 216 square leagues, *i. e.*, about 2,000 square miles, the quantity is of little consequence, and being rather remote, and the quality inferior, it cannot be worked profitably for the present.

The width of the quebracho belt varies a great deal, but it is safe to say that nowhere does it exceed three to four degrees of longitude; its eastern limits are well defined by the course of the Parana and Paraguay rivers, from which it extends westward anywhere from 40 to 325 kilometers—25 to 200 miles—the variation being due to causes which will be referred to later. From this it will be seen this region is far from being an unbroken

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continuous forest such as the Appalachian system carried originally, instead it consists of patches or islands, from a few acres to several square miles in extent, or in long strips or belts of all dimensions, the intervening spaces being great clear levels of grass covered land or swamp.

So much do the stands and other characteristics of this timber vary in the various sections, a description of each province or territory will do much to give a comprehensive and comparative idea of the whole. Beginning with the province of Sante Fe, as having been the scene of the earliest exploitation of quebracho as a tanning material, there was—starting some 30 kilometers from the river, and extending from 150 to 200 kilometers inland at the widest part, and 350 from north to south—originally an area of about 2,100 square leagues[1] or 20,000 square miles bearing quebracho, which at a conservative estimate of 18,000 tons per league gives a total original tonnage of about 37,800,000 tons, the yield per square league varying all the way from 5,000 to 60,000 tons. However, both of these figures are exceptional, and a variation of 10,000 to 25,000 tons will cover the general average. Of the whole area, between 50 and 60 per cent. is really timbered, therefore the actual stand is more dense than the yield per league indicates. To present a clearer picture of the foregoing to those accustomed to North American methods of estimating timber, I may put it this way: the average tonnage per acre of total area is 2.9 tons, or 5.8 tons per acre of actual timber, and as the average log of this section, including limbs large enough to work, weighs 325 kilos—715 pounds—the stand is equivalent to nearly 18 such trees per acre, containing roughly 2,250 board feet, log measure, a comparatively light yield until we take into consideration that these forests resemble our hardwood ones in that they carry usually quite a variety of other woods, such as lapacho, curupay, quebracho *blanco,* goyacan, yacaranda, algrroba, palo *blanco,* etc.,

[1] The Argentine league is 5 kilometers, a square league = 25 square kilometers or 2,500 hectares. One hectare = 2.47 acres. One square league = 6,175 acres or 9.61 square miles. A kilometer is 0.62 mile.

The Paraguayan league is 4.33 kilometers, having been originally 5,000 varas or Spanish yards. A square league Paraguayan is 1,875 hectares or 4,631 acres.

The Brazilian league is 9.68 kilometers or 6 miles.

The Argentine league is used as the standard throughout this article.

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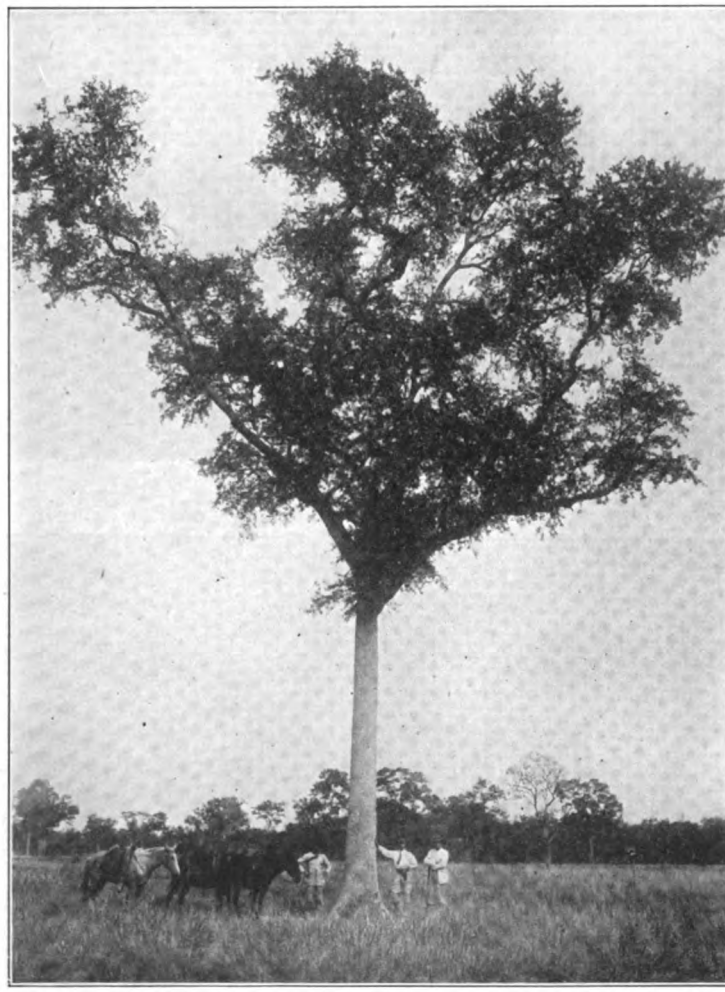
which bring the total up to quite a respectable figure. As a matter of fact it is not unusual to see cut over tracts, which but for the



"Many centuries have elapsed since these trees proved their right of survival." An exceptional quebracho *Colorado* yielding five tons of wood.—Page 201.

absence of quebracho, have every appearance of being virgin timber, although this is not so true of the forests of Santa Fe

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"Far from being an unbroken continuous forest."—Page 173.

"During the working season, the men erect a rude shelter and with their families, live where they work."—Page 193.

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as of some other sections, for it is beyond question that this was the most heavily timbered section of the quebracho country.

The total tonnage figure given above refers to the original or virgin stand, and to arrive at the probable quebracho timber resources as they exist to-day, we must take into account, that in this province quebracho has been cut in ever increasing quantity, for purposes other than tannin, for over 100 years, and that for about 25 years the great bulk of all the tanning extract was made from wood originating in Santa Fe, so to arrive at a reasonable conclusion as to the quantity still standing, it is necessary to make a very considerable reduction. No data exists on which to base an estimate of the cut from the beginning of the 19th century to the present time, but it is certain that until railway construction began in Argentina the quantity was negligible. Since then, however, it has been quite important, growing continuously more so with the advent and extension of the tanning extract industry in Argentina and Europe during the past 25 years. Illustrating this, in 1901 215,000 metric tons of wood were utilized for the manufacture of extract, in 1913 the quantity had increased to almost 750,000 tons. From such data as is available and personal investigation on the ground, the conclusion is reached that at least 15,000,000 tons have been cut for all purposes, which deducted from the estimate of the original total of 37,800,000 tons leaves still available 22,000,000 tons.

Chaco Argentina.

The territory of the Argentine chaco, lying immediately north of the provinces of Santa Fe and Santiago del Estero is rapidly becoming the most important source of quebracho *colorado*. With a total area of upwards of 3,600 square leagues, the forested areas comprise some 2,500 square leagues or 24,000 square miles, *i. e.*, two-thirds of the entire area, and 20 per cent. more than Santa Fe originally carried. The stand of timber, however, is not as a whole equal to that of the province just mentioned, nor is there a like proportion of timber land or *monte* to open *campo*. In this section the timber originally grew to within ten kilometers—six miles—of the Parana river, which is considerably closer than it was found in most places, at present the eastern limit is a few kilometers farther west. From there it extends in

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a northwesterly direction for 300 kilometers—185 miles—or more. Beyond 250 kilometers the stand becomes very light, and the quality as to tannin content slightly inferior. Up to 200 kilometers from the river the stand is heavy and the quality, though not equal to the best Santa Fe wood is very good.

The timber belt, it will be noted is wider here than at any other point in the entire quebracho region, being somewhat analogous in this respect to the chestnut belt of the Appalachians, which widens out at the latitude of Kentucky and Tennessee, extending well west into these states, but narrows to both north and south.

The area extends entirely across the territory from its boundary with Santa Fe to the Bermejo river, separating it from Formosa on the north, the distance being about 50 leagues or 155 miles; thus the forest of the chaco for the most part lies within a block 50 leagues square. Of this area not over 45 per cent. is in timber, which circumstance, by reducing the yield per league fails to convey a correct idea of the density of growth. It is, however, true that even at a very considerable distance from the river, there are leagues carrying as much as from 40,000 to 50,000 tons, on the other hand there are many leagues which will not exceed over 7,500, and a fair general average for the 2,500 square leagues is 15,000 tons per league, giving a total of 37,500,000 tons. Up to the present the cut has been comparatively insignificant, the surface having scarcely been scratched so to speak, and there are still millions of tons within fifty kilometers of the river.

About one-third of the chaco forest is still government or fiscal land, and the other two-thirds privately owned. Being fully cognizant of their value, these fiscal lands are being held to be doled out in small lots to the highest bidder, as financial necessity demands.

Santiago del Estero.

Adjoining and to the west of Sante Fe and the chaco lies the province of Santiago del Estero, the timbered region of which, so far as quebracho is concerned, may be said to carry the westward fringes of the forests of Santa Fe and the chaco. As a factor in the total resources, it cuts little or no figure and while the author has little personal knowledge of this section, the information gathered from those who are conducting logging oper-

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ations there, leads to the conclusion that the timber is both sparse and inferior, and will not exceed 2,000,000 or 3,000,000 tons at most.

Territory of Formosa.

Next to come under consideration is the territory of Formosa. Situated north of the Argentine chaco, and divided therefrom by the river Bermejo, it extends to the Pilcomayo, which forms the boundary between it and the Chaco Paraguayo, a distance of 35 leagues or 110 miles. The timbered area of this territory has not been very thoroughly explored, and though said to be rich in timber, it is a reasonable assumption that the forest extends no further west than it does in the chaco in the south, and in the Paraguayan chaco on the north. Both of these localities being very well known—especially the former—along the Formosa boundary lines, and the knowledge that the stand of timber becomes lighter, and the jungle or underwood and parasitic growths more dense as the tropics are approached, makes it evident the quebracho bearing area does not exceed 1,150 square leagues or 11,000 square miles.

Basing an estimate upon the average of the stands on the northern edge of the Argentine chaco and on the southern edge of the Paraguayan 8,000 tons per square league or a total for the territory of 9,000,000 tons is on the liberal side. Enough is known of this region to warrant the statement that very great areas are not only subject to inundation but consist of permanent swamps or *esteros,* which preclude the presence of timber of any description.

On this account it will be a long time before the forests of Formosa become important to any extent from a commercial standpoint. The territory may be said to be virgin, as the cut up to present is immaterial.

Quebracho in Paraguay.

The quebracho timber belt of this country lies almost entirely in the chaco, which is all that part of Paraguay west of the river of that name. Those familiar with the regions already referred to and also the one now under consideration, have doubtless recognized, that once the Pilcomayo river is crossed going north, a great difference in the character of the forest is encountered.

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Ranging in a broken and desultory way over five degrees of latitude—an approximate distance of 560 kilometers or 350 miles—the width varies from a few kilometers to 80 or 90, but rarely if ever exceeds 100 kilometers or 62 miles. Indeed, it is only in very exceptional instances that the width is so great, therefore, notwithstanding its great length the quebracho producing area does not exceed 1,500 square leagues or 14,400 square miles.

Nowhere in the whole range does the average stand approximate that of the country to the south, and not over 30 per cent. of the area is timbered. As a consequence the yield per league falls to about 3,000 tons or less. A solidly timbered league will not yield at the best over 8,000 tons, and selected areas of the best timber do not average over 4,000 tons. Quebracho has been cut for building and other purposes in Paraguay for several hundreds of years. It is therefore impossible to estimate closely what the original stand amounted to. However, the probabilities are it never exceeded 4,500,000 tons. A million tons will cover the cut up to the present, but ignoring the past, it is a certainty the present resources do not exceed 3,500,000 tons, which in comparison with like areas in the south is insignificant.

Total Resources of Argentina and Paraguay.

Summed up, the total available tonnage of quebracho *colorado* now standing in these coutries is comprised as follows:

Argentina—		
Province of Santa Fe	22,800,000	metric tons
Territory of the Chaco	37,500,000	metric tons
Province of Santiago del Estero	2,000,000	metric tons
Territory of Formosa	9,000,000	metric tons
Total for Argentina	71,300,000	metric tons
Total for Paraguay	3,500,000	metric tons
Grand Total	74,800,000	metric tons

Values of Timber Lands.

The value of the timber lands under discussion, are more or less subject to fluctuation, therefore, such as are now cited can only be taken as true of the past and present. The tendency in Argentina is constantly upward, and there is but little doubt that the next decade or two will witness a great appreciation.

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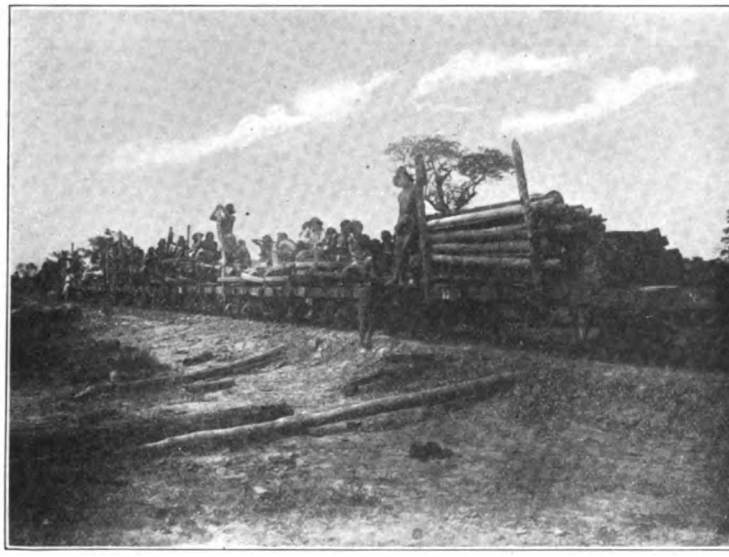
"One may ride for endless leagues through flower carpeted verdant levels. Quebracho on the skirts of the forest, it is impossible to photograph it in the forest."—Page 201.



An empty log train taking a miscellaneous cargo out to the *monte*. The Indians, whom curiosity has brought to the puerto, are being deported to their own hunting grounds in the west.

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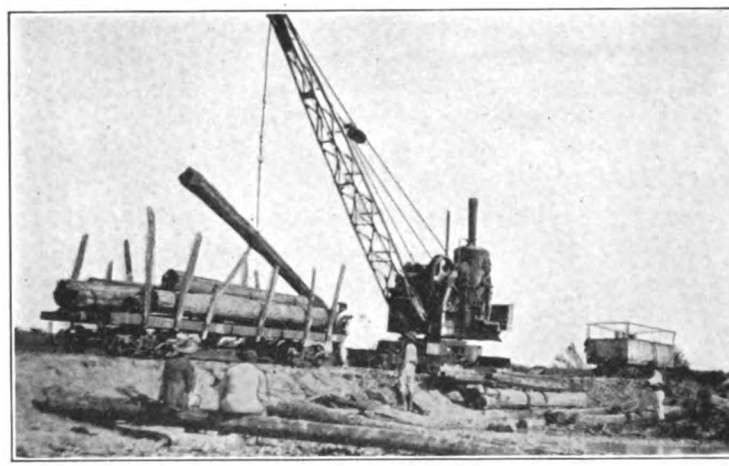
In placing a value upon any given tract, much depends upon whether it is estimated from a timber, cattle grazing, agricultural, or a combination of all three view points. At present, excepting



A wet weather expedient for loading logs. Note water in right foreground. Hauling up skids with oxen or lifting with a hand winch is cheaper on dry ground.

"It is imprudent to rely upon a longer period for stocking the annual requirements of a mill."—Page 197.

in the vicinity of centres of population and transportation there is no great range of asking prices for tracts involving one or more leagues. In Santa Fe there are blocks which would be cheap at

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$100,000 gold per league on account of the timber alone; again where the land is about evenly divided for timber and cattle or agriculture, one-half the above price would be sufficiently high. In the case of land which is low or swampy the value is nominal and much of it would be dear at any price. As a matter of fact, the proprietors of desirable land have not within recent years shown much disposition to sell, under which circumstances real values are difficult to arrive at.

In the Chaco, values have not attained the high levels of the neighboring province, and good timber lands carrying upwards of 20,000 tons of quebracho can be purchased at from $25,000 to $35,000 gold per league. Within the last ten years lands in this section have increased in value tremendously; a block of some 90 square leagues, distant 30 to 60 miles from the river and with a line of national railway crossing its base, sold at government auction ten or twelve years ago for about $7,500 gold per league; to-day this land cannot be bought for less than $35,000 to $40,000 gold per league. Land quite 120 miles inland from the river, purchased twenty years ago for 40 centavos per hectare, or less than $500 gold per league, is now offered at 22 pesos per hectare, which on normal exchange is equivalent to $24,200 per league.

The government lands, which are among the best in the chaco are being disposed of very slowly, and with the idea of meeting only the demands of natural development. In this Argentina wisely recognizes that her forests, which consist mainly of extremely slow growing hardwoods, are practically non-replaceable, and being at best sparsely forested in proportion to her total area, great conservatism is being exercised in turning them over for private exploitation. The method of disposing of these lands has been changed from time to time, but at present the procedure is: after surveying and dividing the allotment to be sold into league blocks to advertise for bids at so much per ton, the bid having to be accompanied by a small deposit as a guarantee of genuineness. On the date specified the timber rights are awarded to the highest bidder, and a further deposit called for to cover payment for the first year's minimum cut, an annual maximum and minimum being established by the government department of forestry. Heretofore timber rights so disposed of have brought 3.50 pesos Argentine paper, *i. e.*, $1.54 gold per

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metric ton, but it is a certainty that future sales will be at very materially higher prices. No one is allowed to bid on more than one league and the sales are not open to companies or corporations, nor can the rights so acquired be transferred. Upon failure to cut or at least pay for the specified annual minimum, the timber reverts to the government. Political influence, however, enters into these transactions to such an extent that considerable latitude is practiced in the direction of those who are so fortunate as to control it.

As to the lands in Santiago del Estero and Formosa, neither a sufficient stage of development has been attained, nor a real necessity for exploitation arisen which warrants valuation, hence any value placed at this time upon the timber lands of these sections would be wholly speculative, and one man's guess as good as another's.

In Paraguay the entire Chaco comprising probably 90,000 square miles—this depending upon where the northern boundary between Paraguay and Bolivia is eventually located—is in the hands of private owners, having been long ago disposed of by the various governments, not infrequently as recompense for financial or other aid in one or other of the many revolutions indulged in by that unfortunate country. A notable instance of this being that of a prominent Argentine capitalist, who for an advance of $300,000 gold was awarded 3,000 square leagues—13,000,000 acres—the cost figuring out in U. S. currency 2⅓ cents per acre. The government maps show this region all nicely divided into rectangular blocks, according to the theoretical disposition as executed in the official engineer's office, but as the Chaco Paraguayo has never been surveyed, nor yet explored except along the basin of the Pilcomayo and for a fringe of 30 or 40 leagues back from the river, the ownership of any specific boundary is much of a moot point. Few of the owners have ever seen their chaco lands and it is very doubtful if they would be able to identify them if they were to see them. However, this matter of division is of no interest to the general reader. From the paragraph on Paraguay's quebracho resources, it will be obvious that as a timber proposition the value is very low, indeed it is questionable if they are ever seriously considered as such by those who know anything about them, the value of the land for grazing

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being the first desideratum, and the quebracho merely incidental. Primarily land values in this section are based upon proximity to the river, elevation as regards inundation, water for stock, and the proportion of open camp.

The present value of land bordering the river and extending inland 10 to 20 leagues—this includes the timbered zone—ranges from $4,500 to $8,000 gold per Paraguayan league of 4,621 acres; this is equivalent to $6,100 to $10,800 gold per Argentine league of 6,175 acres. As to future appreciation in value, as may be gathered, this is a matter that will be controlled by the development of grazing and agriculture.

Physical Aspects of the Quebracho *Colorado*.

As the author is confining his remarks to observations made in the course of actual practice, a botanical description of this tree or its analogies is superfluous here, and if desired may be found in any botanical work on sub-tropical and tropical forest trees.

It may be noted, however, that although the term quebracho is almost universally employed in North America and Europe in connection with quebracho *colorado* on account of its industrial importance, and to a more limited extent applied to a species, the bark of which yields medicinal products, it has no botanical significance beyond having been originally applied to any tree, the wood of which was particularly hard or brittle. The word itself is derived from the Spanish verb *quebrar*—to break, and *hacha*—an axe—axe-breaker. Forest trees are found in almost every Central and South American country, which are locally referred to as quebracho, but which bear no botanical relation to, nor close physical resemblance to the quebracho of other countries.

Compared with its North American parallel—the chestnut—the condition under which the quebracho *colorado* flourishes and attains its greatest commercial value are quite circumscribed. Stretching from north to south over a range of latitude equal to that covered by the chestnut belt, the climatic conditions where quebracho grows most prolifically are much more uniform, especially with regard to temperature. By far the best stands of timber are found between latitudes 27° 30′ and 31° S., where the temperature rarely exceeds 105° F. (40.5° C.) in summer and seldom falls below 28° F. (—2.2° C.) in winter, as against 95° F.

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(35° C.) in summer and as low as 15° F. (—26° C.) below zero in winter for the chestnut region, the effective difference lying in the temperature below the freezing point.

A notable feature is that the quebracho and chestnut richest in tannin grow in the southern extremities of their respective zones, the isotherms of which do not differ greatly, but, whereas the quebracho deteriorates towards the equator, chestnut does so as it becomes more remote from it. In the latter case, climate is no doubt an important factor, but the same cannot be said of quebracho, the deterioration being distinctly due to other causes. With chestnut altitude has a very marked effect upon the tannin contents, being equivalent to a latitudinal or climatic difference, but a thousand feet higher or lower in the same general locality is not noticeable, and the tree itself develops in dimension, and is as thrifty on a mountain top as on the lower levels. Quebracho, however, appears to be very susceptible to variations in levels so limited, that it is rarely if ever seen on an elevation as little as 50 feet above the surrounding plain, and this no doubt is a prime cause for its running out, at short distances from the rivers which it borders, instead of spreading over the entire pampa, of which the general level rises 9 to 10 inches per mile towards the west.

It is not the higher level in itself which affects the growth, but in the author's opinion, the difference in the moisture content of the soil. Observations tend to the conclusion that the balance in the moisture requirements of the quebracho tree is extremely delicate, but regarding this it must be explained, the soil of the pampa region is practically impervious to water, hence it is from surface flow and not by permeation or percolation that drainage is effected. A difference of a few feet in level will cause the soil to be almost arid in one spot, and a swamp or pond in the adjoining one. Neither of these conditions are conducive to the growth of quebracho, and as the jump from one to the other is not more than a few feet, it becomes apparent that favorable soil conditions for its growth are confined to limits, which in a North American forest would never be noticed.

The existence of great levels in Santa Fe and also in the chaco Argentina, which drain slowly enough to furnish the necessary moisture to the tree and yet with sufficient rapidity to obviate long or frequent inundation accounts to a great extent for the superior

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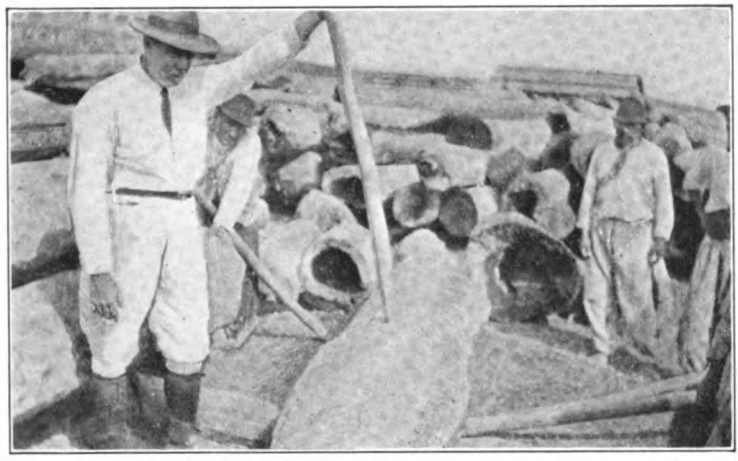
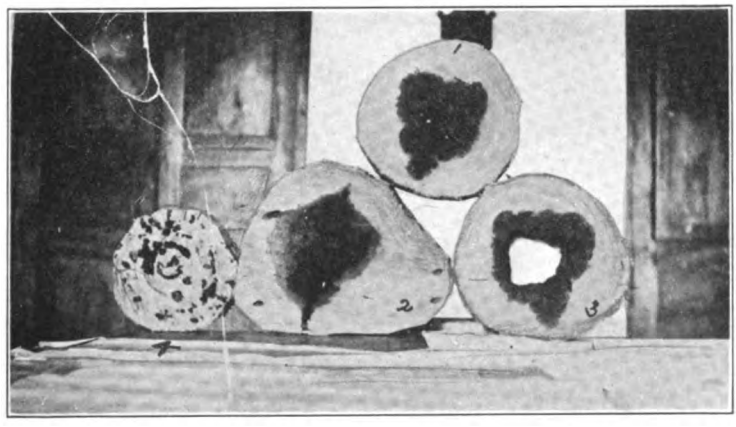
stands of this timber in these sections; on the other hand it is the lack of them which has prevented it from attaining perfect development in Formosa and notably in Paraguay.



"A barrel-like swelling about midway of the trunk."—Page 191.



Sections 1, 2, 3—"The rot begins at the heart of the bole where the major roots spread." Section 4—"A secondary source of rot * * * is induced through the medium of a huge bore-worm."—Page 190.

Beginning north of the Bermejo river and continuing on to the swamps of Puerto Suarez in the southeast corner of Bolivia, the greater part of the country is subject to frequent inundation, and this is not confined to the *esteros* or low grounds, as the author

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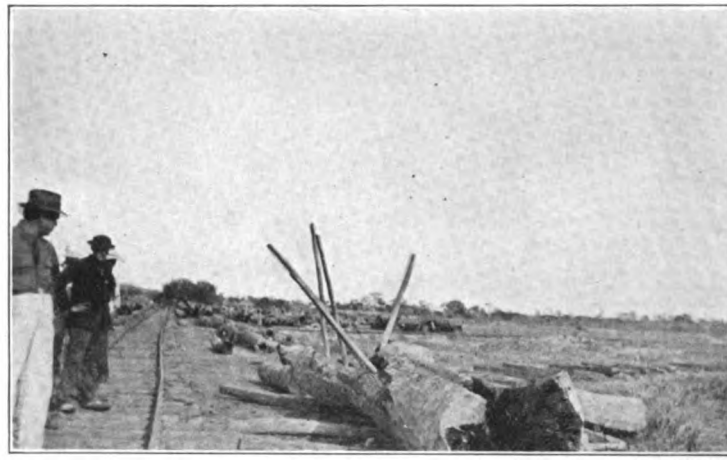
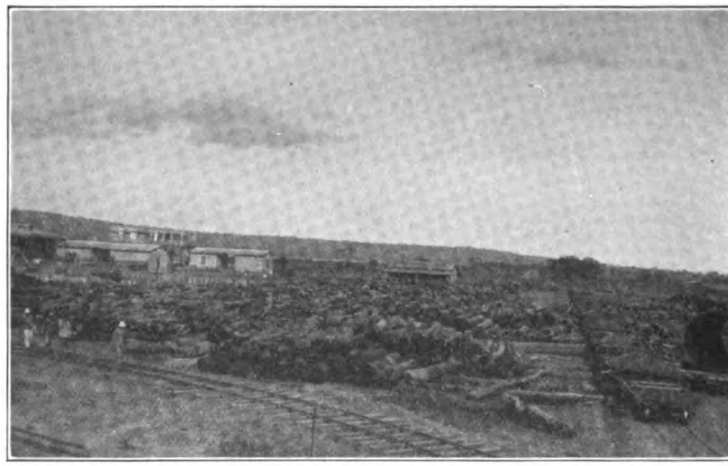
has at various times ridden many leagues where the forest was from 2 to 3 or more feet under water. These floods are not al-



"The rot * * * extends upward * * * converting the trunk into a mere shell."—Page 190.



Part view of a log yard.

together the results of local rainfall, but oftener are the result of the overflow of the river Paraguay, caused by the tropical rains many hundreds of miles to the north in Brazil. In fact great

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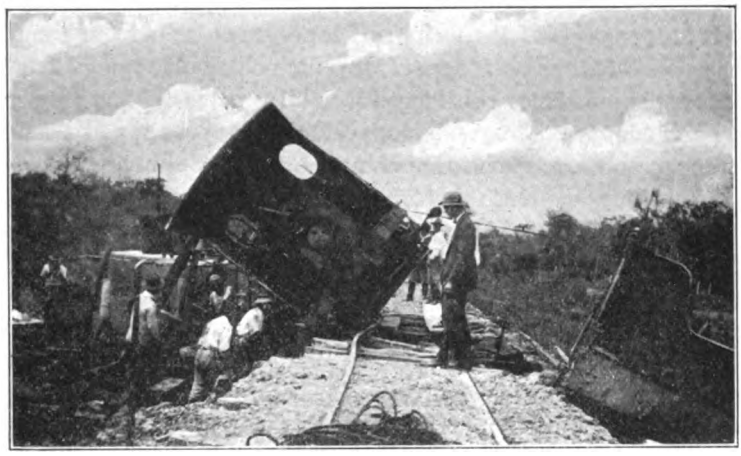
tracts of the Paraguayan chaco are often inundated where rain to speak of has not fallen for months.

Whether by reason of climate, or moisture, or both, there is a very marked difference in the character of the timber north of the Bermejo; in the Argentine the tree boles are comparatively short and thick, and the limbs heavy and of great spread, the limb-wood yielding from 10 per cent. to 15 per cent. of the total weight of the tree. In Paraguay the boles are long and slender,



"Not always can the ties and rail be kept from sliding off the roadbed."—Page 200.

straight logs averaging between 7 and 8 meters (23 feet to 26 feet) in length as against 5 to 7 meters (16 feet to 23 feet) in Argentina, but the limbs as a rule are not of sufficient value to pay the cost of cleaning and hauling. The most important difference between the timber of the north and south consists of the yield of merchantable timber, or the proportion rendered worthless by heart-rot.

In the south, about 10 per cent. of the trees are so affected, whereas in Paraguay upwards of 60 per cent. are decayed at the heart to a greater or less extent, many apparently sound, thrifty trees being rot-filled shells, a fact that is not always discovered until the axe is applied. During a careful examination of the stock on the yard of an Argentine tanning extract plant, where

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30,000 tons of logs were piled so both ends could be inspected, less than 100 were found showing evidences of having had the decayed portion cut off; of course there may have been many which were trimmed above the point of decay, still the yield per league of merchantable timber is rather conclusive evidence that the loss from this cause does not exceed 10 per cent. of the total tonnage. As against this, if Paraguayan logs destined for timbers, sleepers, or extract manufacture were trimmed in accordance with Argentine practice, the loss would be at least 50 per cent. Figures given by an old established Paraguayan extract plant, show that 20 per cent. of the weight of the logs as brought to the mill was discarded. These figures do not include trimming done in the woods, nor trees considered worthless after felling. Reverting for a moment to yields and values, it will be noted that the merchantable quebracho timber north of the Bermejo, for equal areas, is only one-tenth that of Argentina.

The causes of decay appear to be similar throughout the whole quebracho region, and so far as observed, there are two principal ones. Where trees are standing on ground which has become chronically saturated with moisture, the rot begins at the heart of the bole at the point where the major roots spread, and gradually extends upward, eventually converting the trunk into a mere shell; occasionally it continues from the trunk into the larger limbs. Trees of all sizes and ages are equally subject to it, and the author has noted its existence in young trees not over eight inches in diameter. A secondary source of rot is that induced by the introduction of moisture and fungoid infection to the interior of the tree through the medium of a huge bore-worm some three inches long and half an inch in diameter, which leaves a bore equal to its own size. These bores are sufficiently large and numerous to permit the washings during heavy rains to enter, and also provide a receptacle for wind-blown and insect borne fungus spores; trees thus attacked succumb very quickly and completely. The absence of laboratory facilities prevented any attempt to determine whether fungi or moisture alone was the immediate cause of this decay, but it is quite apparent a considerable excess of moisture is necessary for its promotion. A third but minor cause may be the lodgement of parasitic growths in the crotches of the main limbs, but as the period of observation did

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not permit of determining whether the rot or the parasite was there first, there is room for doubt.

Decay from the outside is never seen, in fact quebracho *colorado* is considered indestructible, even under trying conditions, railway cross-ties and dock timbers which have been in service forty years or more, are, except for surface weathering as sound as when installed, and it is said to resist the *teredo* or ship-worm so destructive to submerged piling in tropical or sub-tropical waters. The foregoing circumstances rather point to fungi as being the chief factor of disintegration of the growing timber. The accompanying photographs illustrate the effect and progress of the decay beginning at the roots, and also that originating in the bore of the worm referred to; attention is also called to the photograph showing a log with a barrel-like swelling about midway of the trunk, this phase is quite common, and is caused by the infection (through worm bores) and decomposition taking place between the root and top. The swelling occurs only after the decay has proceeded to the point of leaving this portion of the trunk a mere shell 1 or 2 inches thick, and is caused by the absorption of moisture by the dust-like cellulose inside.

Forest Operations.

When one who has experienced the joys of getting logs or cord wood out of the rugged mountain fastnesses of Virginia, North Carolina, or Tennessee, first views the pampaen forest, a desire for an opportunity to exploit a logging job as simple and easy as this appears to be, is almost inevitable; a country level to the point of monotony, no inaccessible mountain steeps, ravines, or brawling boulder strewn water courses to encounter and overcome with roads and railways precariously perched upon hillside cuts, no bridges and trestles to be continuously bolstered up, nor geared locomotives running away round 18° curves and down 4 per cent. grades on a slippery track; no wonder it makes a strong appeal to those who may have had to contend with the Blue Ridge or the Great Smokies. From a topographical and climatic point of view, it indeed seems a veritable woodsman's paradise, but while comparison is in favor of the pampa, the South American forest has its problems.

Logging is almost invariably done by contract, the individuals so engaged being usually in the business on a large scale as it

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involves the investment of considerable capital in equipment. Contracts are based upon a price per ton alongside rail, and the contractor assembles his own labor, and as a rule furnishes the necessary live-stock, wagons, tools, and the other thousand and one appliances necessary; in the north (Paraguay) the operators are not infrequently obliged to furnish all the equipment and finance the operations owing to the lack of contractors with sufficient capital to carry on the work.

The tannin extract companies with one or two exceptions depend upon their own timber holdings for a considerable proportion of their raw material, but also purchase logs on the open market as occasion warrants. This is deemed a necessary precaution against possible wet seasons, limited forest reserves, etc., and provides a market for sufficient logs to maintain the existence of private organizations whose sole business it is, at the same time the maintenance of their own forest operations exerts a stabilizing effect upon prices.

Logs for extract manufacturing have in the past been graded into five classes, locally termed in the order of their value, *Exportacion,* consisting of sound, comparatively straight logs, *Typo Fabrica,* sound but ill adapted for export shipment, with perhaps occasional traces of rot, *Ragone,* equivalent in the States to laps and limbs, *Pica* or *Podrido,* worm-eaten and more or less rot, and *Campana,* fallen timber from which the bark and sap-wood has disintegrated.

Price is a matter of bargaining between buyer and seller. Prior to 1915 in Argentina logs were laid down alongside rail, for from 6 to 8 pesos, *i. e.,* $2.65 to $3.50 per metric ton, with somewhat lower figures for the inferior qualities, the cost delivered at mill depending upon the railway haul. Since then the increased cost of operating has sent the price up to from 18 to 22 pesos, *i. e.,* to about $8.00 to $10.00. In Paraguay the prices have always been higher, and during 1920 were from $10.00 to $12.00 at river bank.

Until 1915 or 1916 the grading of logs was quite strictly observed, and large stocks of export material were accumulated for some time after the European conflict had brought exportation to a close, but with little or no prospect of a resumption of quebracho extract manufacturing in Germany—its principal seat in Europe—the necessity for classifying the two or three first

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grades disappeared and the mills are now receiving what might be termed forest run, the average quality being decidedly better than it was a few years ago. The foregoing applies wholly to Argentina, as in Paraguay the difficulty extract plants and saw mills experience in securing an adequate supply of raw material precludes the development of an export trade in this direction.

In opening up a boundary of quebracho forest, the procedure is similar to that practiced elsewhere, the first work being to clear out roads about 4 or 5 meters wide and running parallel one kilometer apart, this is done by men directly employed by the contractor; from these roads intersecting *picadas* or narrow pathways are cut dividing the territory into blocks approximately one kilometer square, the felling and log cleaning upon which is subcontracted to individuals or small contractors employing a small number of men who in turn work by the ton. After felling, the trunk and limbs large enough to warrant it are stripped of bark and white sap-wood, leaving only the clear tannin carrying redwood. The bark and sap-wood vary greatly in thickness, being anywhere from 1 to 3 inches, the size or age of the tree being no indication of this. The cleaning which is accomplished by hewing this outside off in splinters lengthwise constitutes four-fifths the labor of the axeman. Men on this work, fell and clean on the average about 15 tons per month per man. During the working season, the men erect a rude shelter and with their families live where they work, all food, clothing and other supplies being sold to them by the contractor. He in turn frequently is compelled under his contract to purchase from the company for whom he is logging, with the result that the cost of the work to both, virtually amounts to what it costs to maintain the men and their families.

After the logs are cleaned they are measured, the weight computed from the cubic contents and the amount credited up to the axeman, the contractors private mark is then stamped or painted upon the log, which is then ready to be dragged to the nearest hauling road. Here they are picked up by wagon and hauled to the *playa* alongside the railway.

The hauling is done by oxen—two pairs to the wagon—experience having demonstrated their superiority to horses or mules in

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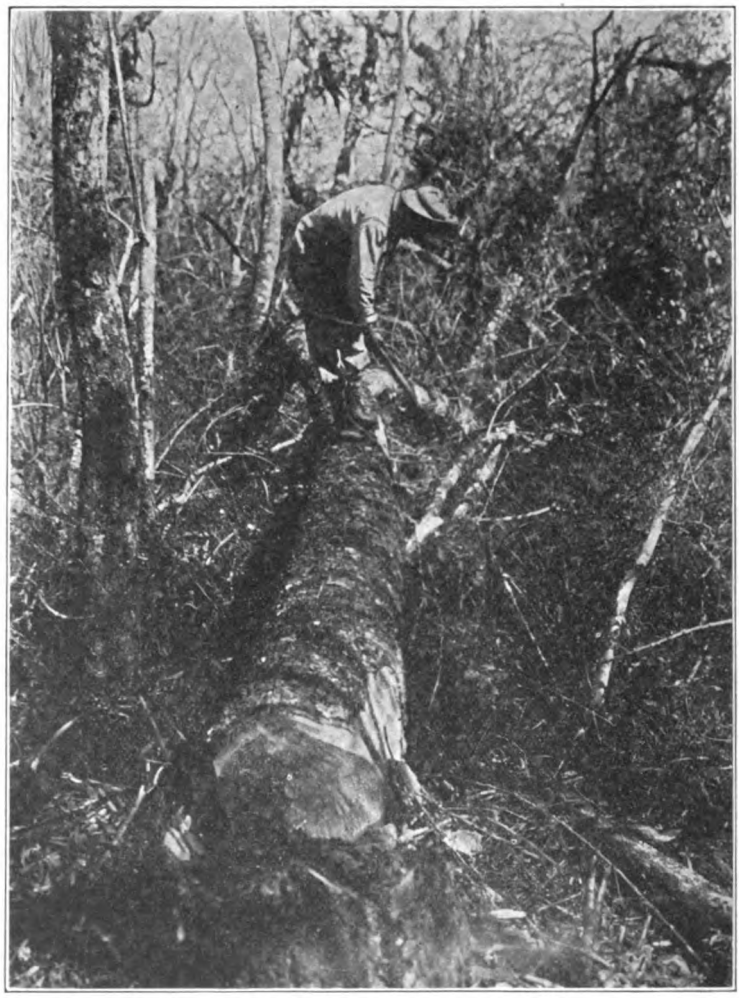
both effectiveness and cost, for grazing on the open camp, the upkeep is practically nil, and when beyond working, they are, after fattening up, worth what they cost as beef for the men. In



"After felling, the trunk and limbs * * * are stripped of bark and white sap-wood."—Page 193.

Argentina the four wheeled wagon (*quechepe*) is most generally employed, but in Paraguay where muddy roads are more preva-

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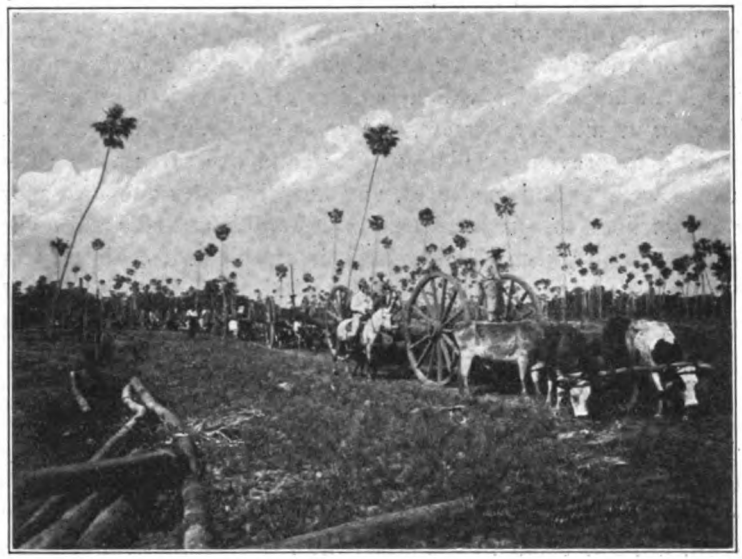
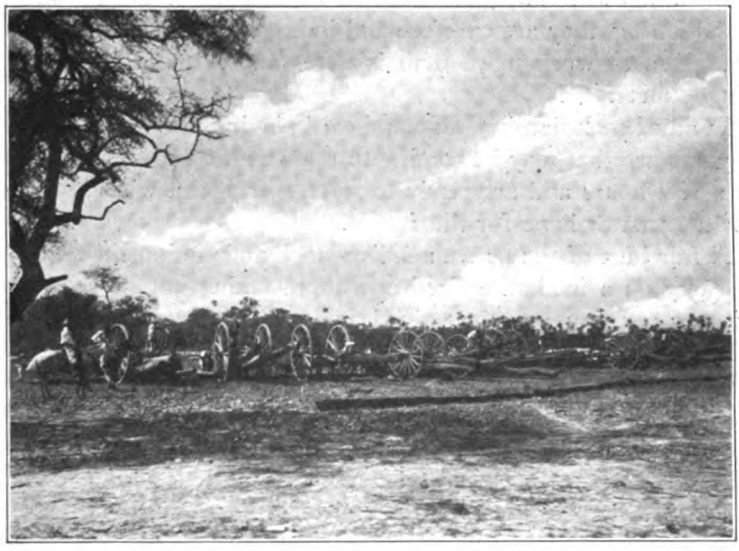


"The hauling is done by oxen—two pairs to the cart."—Page 193.



"Hauled to the *playa* alongside the railway."—Page 193.

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lent, and there is no limb wood to haul, the 8-foot two-wheeled timber cart (*alzaprima*) is still proving its greater adaptability.

The organization of a successful woods operation in these countries is an undertaking which requires all the strictness and precision of a military system, the most stringent supervision is requisite to prevent peculation, graft and deception with reference to weights and measures, and keep in order an outfit more or less inclined to—*fiestas*, let us say. Both contractor and owner must constantly keep reliable staffs in the field, checking up the live-stock and equipment for in the mind of the simple peon, to say nothing of those higher up, the line between *meum* and *tuum* is somewhat hazy.

With regard to labor—the system is distinctly that of peonage—it is plentiful and for the most part recruited from the peon class, who are essentially, with perhaps a slight mixture of Latin blood, descended from the aboriginal Indian of the country; in intelligence and general qualifications they are superior to the southern negro, but not equal to the emigrant from southern and southeastern Europe who in considerable numbers augment the ranks in the slightly more important classes of work; simple minded, their wants are few, good natured though quick to provoke to blood-letting, they are carefree and irresponsible to a degree, and not given to work more than is necessary to make buckle and tongue meet.

Fond of cock-fighting, *tava* and card playing, they gamble away any balance that may be coming to them at the end of the month in a few hours and are ready to start over again, without regret for the past or hope for the future.

A fair idea of the personnel, live-stock and equipment required to carry on a moderate sized operation, taking out say 200 tons of logs per day may be gained from the following tabulation, which is subject to modification according to whether the haul is longer or shorter than an average of one and a half leagues; the figures given, however, are based upon actual operation under normal conditions.

As the men are invariably accompanied by their families, there are at least 3,000 men, women and children to feed, clothe and administer to; not a small task in these remote regions, as for instance, the item of beef alone for such an outfit as that above cited requires the product of a herd of 25,000 cattle.

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Superintendent and assistant	2
Foremen	10
Storekeepers and assistants	6
Carpenters and blacksmiths	12
Axemen	350
Log cart drivers	100
Herding and caring for oxen	10
Sundry labor	20
Total for logging	508
Subsidiary work such as getting out fence posts, cross-ties and fuel wood	100
Grand total	608

The capital investment in live-stock and equipment for such an operation is represented by the following list:

Oxen, fully broken	2,000 at	$65.00	$130,000
Young steers being broken for replacement	500 at	45.00	22,500
Horses (saddle)	100 at	35.00	3,500
Log wagons	150 at	150.00	22,500
Box and water carts	40 at	65.00	2,600
Tools, chains, etc., etc.			10,000
Spare parts and repair material			5,000
Carpenter and blacksmith shops			2,500
Total			$198,600

The duration of the working season depends entirely upon the weather, and to a considerable extent in some localities upon how prevalent mosquitoes and *pulverinos* are, for there are periods when human existence is made unendurable by these pests, especially is this so in Paraguay—the land of *bichos*. Extremes of either drought or wet effectually put a stop to all work involving the use of live-stock, the former on account of insufficient water and pasture—it requires 12,000 to 15,000 acres of natural grass land to graze the live-stock for an operation as given above—while in wet weather the roads become bottomless canals of liquid mud in a very short time. A fair estimate, perhaps, would be nine months of the year for Argentina and not to exceed seven in Paraguay. In any event it is imprudent to rely upon a longer period for stocking the annual requirements of a mill.

Transportation.

For the transportation of logs to extract plants and saw-mills both rail and water routes are available, although the latter is employed to a rather limited extent and only when logs are

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A water and supply train distributing food and drink—*agua fresca*. Note the square water tank cars.

"The 8-foot two-wheeled timber cart—*alzaprima*—is still proving its greater adaptability."—Page 196.

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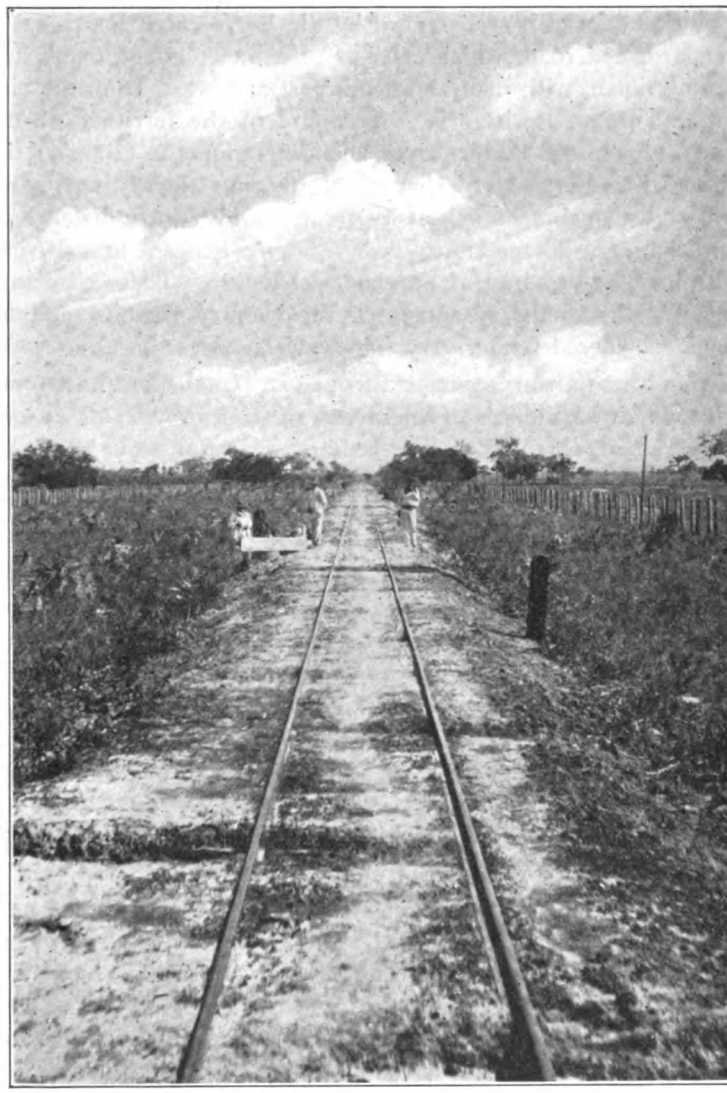

"A certain degree of permanency is attained by covering the cross-ties * * * with earth, leaving the surface heavily cambered and drained at each rail joint."—Page 200.

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brought from remote places where there are no railways. The Argentine district is well served by the Ferro-carril Santa Fe, a French owned road, which consists of a meter guage trunk line running north, with many branches east and west, from the city of Santa Fe to Resistencia, the capitol of the territory of the Chaco. From the Parana river near Barranqueras (Balilla) the national line Ferro-carril Central Norte runs slightly northwest through the quebracho belt at its greatest width for a distance of more than 200 kilometers to Teday, from whence a branch runs south into the province of Santiago del Estero. These roads are as well built as the resources of the country permits, and all things considered render very fair service.

From these trunk systems the private companies have constructed many hundreds of kilometers of 60-centimeter or 24-inch guage railway running to the scene of operations, one company alone having approximately 300 kilometers of such lines, and nowadays, it is only rarely anyone hauls by oxen more than the distance of three leagues.

In Paraguay, practically all transportation of logs is over the lines built by the owners of the plants which without exception are located immediately on the river; these railways of course run only from the plants to the forest, and serve in no way to connect up one place with another. Several companies whose reserves or equipment are not sufficient to stock their mills, transport such purchases as can be made by water exclusively, and all logs and timber destined for export are conveyed to the Parana and Paraguay rivers by rail and thence via water to the deep-water ports.

As may be surmised the construction of railways in the quebracho region is a comparatively simple matter; grades are unknown and circuitous routes unnecessary, while the erection of bridges or trestles presents no real difficulty. The fly in the ointment—for there is one—lies in the absence of material suitable for setting up a permanent roadbed. Stone or gravel does not exist anywhere in the whole region, hence the alluvial soil is perforce employed. In wet weather it rapidly acquires a soap-like consistency, which makes the maintenance of levels impossible, and not always can the ties and rail be kept from sliding off the roadbed altogether. A certain degree of permanency is attained

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by covering the cross-ties to the level of the ball of the rail with earth, leaving the surface heavily cambered, and drained at each rail joint. To maintain these roads in serviceable condition constant labor and attention is necessary, for once water gets under the cross-ties, the bed will melt away like soap.

The General Aspect of the Forest.

Having dealt with the commercial phases of these forests, a brief afterword of general description supplementary to that at the beginning of this article may not be considered amiss.

It is in the early summer, for there are really but two seasons down there, the forest of the pampas is at its best. If the season has been normally moist one may ride for endless leagues through flower carpeted and verdant levels, among islands and miniature continents of woodland in a combination which rivals in interminable variety of extent and vista the most beautiful of carefully nurtured park lands.

Primordial in aspect and primordial in fact, for many centuries have elapsed since thousands of these trees first proved their right of survival by lifting their evergreen crowns above the impenetrable jungle of sub-tropical vegetation and parasite. As though existing in dread of the day when the woodsman's axe would dispute their right to live on, it would seem as if they, the monarchs, had reared their heads on high and then surrounded themselves with an armed force to defy the attacks of the god utility. From the lowly caraguaty to the 20-foot cacti, not excluding the tangled drapery of vine and creeper, everything that grows seems, with spike and thorn, to be on the defensive, and woe betide the man who has the hardihood to attempt to force their barriers without the ruthless services of the *machete*. Beholding them one feels instinctively, here are the haunts of the jaguar, puma and *gato de monte*.

If the grasslands remind one of the disordered profusion of an old-fashioned garden, the glories of the flowering shrubs, and great blossoming trees would furnish a fitting subject for the pen of a poet, or the brush of a Maxfield Parrish, for the riot of color is more like the stuff dreams are made of than prosaic reality. In groups and singly, the cerulean blue of the *lapachos*, cerise and pinks of the *palo rosa*, the blood warm oranges and reds of the acacias and yellows of the *para todas* form a picture which

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requires a more skilled pen than the writer's to do justice to. A single stem from any of these trees is almost an armful of blossom.

Wild animals, game and birds though in great variety, are not, excepting the predatory species, numerous; any lack in this respect, however, is made up for in others, for there are times when either artist or philosopher would have difficulty in appreciating the scene with the calm, born of the silent places of the earth, and in the midst of these marvels of generous nature, one too often is exposed to the torture of the *pulverino*, a microscopic sand fly, which rises from the ground in clouds like morning mist, and which to get a taste of human gore will penetrate all but the finest of *mosquiteros*, while a not unknown occurrence is for one's horse to lie down under the saddle to roll the mosquitos off, so numerous do they become at times as to make vision or conversation impossible, not only do they get in one's eyes, ears and hair, but in the mouth when it is unwarily opened. Despite these discomforts the country is healthy when life is lived in the open, and binds many to it with the never fading charm which vastness of space holds for mankind.

IRON TANNAGE.

By Daniel D. Jackson and Te Pang Hou.

[*Continued from page 159*]

SECTION V. ON THE RELATION OF BASICITY TO STABILITY IN IRON LIQUOR.

The instability of an iron liquor, or rather, the ease with which hydrated ferric oxide separates out from a solution, depends upon the degree of acidity of the solution. The liquor used in tanning is normally more alkaline than that which corresponds to a neutral salt, *e. g.*, $Fe_2(SO_4)_3$. The liquor, however, reacts acid even when it is constitutionally basic. If an alkali is introduced, the OH^- ions from the alkali tend to precipitate ferric iron as ferric hydroxide or as some basic ferric compound, but the supernatant solution still reacts acid. Only after all the ferric iron has been precipitated, does the solution begin to react alkaline.

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It is evident that in order to study the stability of an iron liquor with regard to its basicity, it is necessary to know quantitatively the relation between the Fe^{+++} ion in solution and the acid radical or radicals present. The subject presents some difficulty, as the acid radical in ferric sulphate solution may be composed of, besides the sulphate ion $SO_4^=$, such other negative ions as NO_3^-, Cl^-, etc. This is not uncommon as the ferric sulphate in commerce is generally obtained by the oxidation of copperas with HNO_3 and H_2SO_4, some of the HNO_3 may remain in the ferric salt solution formed. In order to eliminate as much as possible complexities of this nature, there was chosen as the starting point a white powder of ferric sulphate as nearly chemically pure as possible. A solution of this salt (which dissolves very slowly in water) was made containing 133 g. of the air-dried powder to a liter. The solution was allowed to stand in a closed bottle for four weeks, when a small amount of precipitate collected at the bottom. The solution tested for Cl^- with $AgNO_3$ solution gave a negative result. It was then tested for NO_3^- by adding concentrated H_2SO_4 and then ferrous ammonium sulphate solution. No colored ring was observed. This test is not very delicate. With diphenylamine in H_2SO_4 solution a violet to blue coloration is observed, but as the solution contains ferric iron this test for NO_3^- in the presence of iron can not be regarded as conclusive.[25] The test was therefore further elaborated by distilling with ferrous sulphate and H_2SO_4 and receiving the distillate with a 50 cc. 3 per cent. NaOH solution contained in a 250 cc. Erlenmeyer flask. The distillate was acidified and shaken with 5 cc. of chloroform after adding 5 cc. of 10 per cent. KI solution.[26] The test gave a negative result for NO_3. After obtaining conclusive negative tests both for Cl^- and NO_3^-, it was then necessary to determine the quantitative relationships between the ferric iron and the sulphate radical in the solution. For this purpose a 50 cc. portion of this ferric sulphate solution was diluted to 500 cc., 25 cc. of which were taken for each of the analyses described. In order to establish the quantitative relationships accurately it was considered advisable to determine the iron and the acid radical ($SO_4^=$) each by two independent methods. Iron was deter-

[25] See Tradwell-Hall, Analytical Chemistry, Vol. I, p. 394 (1916).

[26] See A. A. Noyes, Quantitative Chemical Analysis, (1915) p. 113.

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mined gravimetrically by precipitating with NH_4OH in the presence of NH_4Cl, and independently again by the Zimmermann-Reinhardt volumetric method. The $SO_4^=$ radical was determined gravimetrically by precipitating with $BaCl_2$ in HCl solution and independently again by the acidity determination by titrating in the heat against N/10 NaOH, using 1 cc. ½ per cent. phenolphthalein solution as an indicator. In each analysis at least two portions were carried and the results checked. The results were tabulated as follows:

TABLE II.—RESULTS OF ANALYSES FOR Fe^{+++} AND $SO_4^=$ BY INDEPENDENT METHODS.

	Method of determination	No. of equivalents contained in the 25 cc. (dil. solution)
Fe^{+++}	Zimmermann-Reinhardt	0.003853
	Gravimetric as Fe_2O_3	0.003866
$SO_4^=$	Gravimetric as $BaSO_4$	0.003861
	Titration against N/10 NaOH	0.003872

NOTE. 1.—The Zimmermann-Reinhardt method is not suited for H_2SO_4 solution because (1) the ferric sulphate solution in the presence of H_2SO_4 has a less pronounced yellow color to guide the reduction by $SnCl_2$, (2) the reduction by $SnCl_2$ is much slower in the H_2SO_4 solution than in the HCl solution, and (3) in the H_2SO_4 solution a precipitate is more liable to form in the solution during the reduction unless a large excess of the H_2SO_4 is present. H_3PO_4 alone without $MnSO_4$ and H_2SO_4 was used. The result was found to be slightly affected by the amount of excess of $SnCl_2$ employed.

NOTE 2.—In the acid determination by titration with NaOH, the difference between the end points in the cold and in the heat is not great, being about 1 per cent. of the total burette reading in the case of ferric sulphate solution and 1½ to 2 per cent. in the case of ferric chloride solution. It is remarkable to note that the corresponding difference in the case of chromic chloride solution is as much as 10 per cent. of the total burette reading.

By "No. of Equivalents" is meant the number of equivalent weights of Fe^{+++} and $SO_4^=$ contained in the above 25 cc. of diluted ferric sulphate solution, so that if the solid ferric sulphate from which the solution was made is chemically pure, *i. e.*, contains nothing but $Fe_2(SO_4)_3$ and water, the number of equivalent weights of Fe^{+++} (which represents 3 equivalents per formal weight) should be exactly equal to that of $SO_4^=$ (which represents 2 equivalents per formal weight). The ratios of the number of equivalent weights of Fe^{+++} and $SO_4^=$ in the solution as determined are as follows:

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TABLE III.—Ratios of Equivalents of Fe+++ to Equivalents of $SO_4^=$ in Ferric Sulphate Solution.

	$SO_4^=$ by gravimetric	$SO_4^=$ by titration
Fe+++ by Zimmermann-Reinhardt	1.000 : 1.002	1.000 : 1.005
Fe+++ by Gravimetric	1.000 : 0.998	1.000 : 1.002

The closeness with which the above results agree indicates that the ferric sulphate employed is substantially chemically pure. Knowing the exact constitution of the ferric salt solution it was then necessary to study the stability of the ferric salt in solution by changing the degree of basicity. This was done by adding a calculated amount of Na_2CO_3 solution of a known strength to a given quantity of $Fe_2(SO_4)_3$ solution and finally making up to the same total volume with distilled water in each case. In this study there was employed a strength of the ferric salt solution in each case not far from that of the iron liquor used in the actual drum tanning operation. This was estimated to be from 2 to 4 per cent. iron calculated as $Fe_2(SO_4)_3$. In this connection it might be added that Na_2CO_3 was used rather than NaOH, as in actual practice in the tannery sal soda or sodium bicarbonate is generally used for such a purpose. A 0.5000 N Na_2CO_3 solution was made from a thoroughly dried, anhydrous C. P. sodium carbonate. For study, a 25 cc. portion of the above ferric sulphate solution containing 10.26 g. $Fe_2(SO_4)_3$ per 100 cc. was taken, a calculated quantity of this Na_2CO_3 solution run in from a burette, and the total volume made up to 65 cc. with distilled water. The results were tabulated in Table IV. Although during the introduction of Na_2CO_3 there was a brisk evolution of CO_2 gas, there remained in the suspension some $CO_3^=$ ions in addition to the OH^- ions, so that the precipitate formed was in the nature of a basic ferric carbonate or a mixture of ferric hydroxide and ferric carbonate.* It was noted that the precipitate separated out from No. 7 more readily than it did from Nos. 8, 9, 10, and 11. It is clear that the ferric sulphate solution having a basicity higher than that which corresponds to No. 6 is unstable and a yellow precipitate of

* To determine how much $CO_3^=$ is present in the suspension, CO_2 was distilled from it after the precipitate had just separated out, with excess of H_2SO_4 and received in a known NaOH solution. Titration gave the amount of $CO_3^=$ present in the suspension to be 63.6 per cent. of the total added.

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TABLE IV.—25 CC. SOLUTION CONTAINING 10.26 G. $Fe_2(SO_4)_3$ PER 100 CC. WITH ADDITION OF A CALCULATED AMOUNT OF N/2 Na_2CO_3 SOLUTION AND DILUTION TO A TOTAL VOLUME OF 65 CC.

No.	Cc. Na_2CO_3 added N = 0.5000	Cc. water added to make up 65 cc.	Basicity ratio $\frac{\text{Equiv. } Fe^{+++}}{\text{Equiv. } SO_4^{=}}$	Color of sol. obtained	Time ppt. begins to form after adding Na_2CO_3	Appearance overnight (18 hours)
1	0.00	40.00	1	Straw yellow	———	Clear solution
2	2.66	37.34	29/28	Yellow	———	Clear solution
3	5.14	34.86	15/14	Red-yellow	———	Clear solution
4	8.57	31.43	9/8	Red	———	Clear solution
5	11.02	28.98	7/6	Bright red	———	Clear solution
6	12.86	27.14	6/5	Bright red	Turbidity first noticed after 50 min.	Bright red sol, with some yellow ppt.
7	15.43	24.57	5/4	Deep red	Ppt. after 12-15 min.	Bright red sol. with more yellow ppt.
8	19.29	20.71	4/3	Deep red	Ppt. after 15-20 min.	Bright red sol. with more yellow ppt.
9	25.71	14.29	3/2	Dark red	Ppt. after 25-30 min.	Red sol. with much yellow ppt.
10	30.86	9.14	5/3	Very dark red	Ppt. after 25-30 min.	Reddish-yellow super. sol. with yellow ppt. (1/5 of total vol.)
11	38.57	1.43	2	Black-red	Ppt. formed after addition, disappears on shaking. Ppt. after 25 min.	Yellow super. sol. with yellow ppt. (3/4 of total vol.)
12	46.30	——*	5/2	Black-red	Ppt. formed after addition, disappears on prolonged shaking. Ppt. after 20 min.	Light yellow super. sol. with yellow ppt. (4/5 of total vol.)

* The total volume of this solution is 71.30 instead of 65 cc.

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$Fe_2O_3.xH_2O$ or some basic ferric carbonate soon separates out. It was found from the tanning experiments also that this degree of basicity in the case of a sulphate liquor was as high as could safely be employed without danger of causing a yellow precipitate to separate out on short standing and also that if the iron liquor employed was of a higher basicity than this, it would rapidly impart a yellow color to the surface of the pelt after drumming from 15 to 30 minutes.

Because of the purely scientific interest involved NaOH was also used in place of Na_2CO_3 so that in this case only OH^- ions were introduced and the complication of having some $CO_3^=$ ions present in the solutions was eliminated. The results are shown in Table V. Comparing Table IV and Table V, it is remarkable to note how the two series run parallel to each other. Table V like Table IV also indicates that in the case of the sulphate liquor Nos. 6 and 7 represent the highest basicity beyond which the iron liquor yields much precipitate. The difference between the two series is that in the case of Na_2CO_3 any precipitate first formed can be caused to disappear on continued shaking to a thick solution from which the final precipitate appears after a lapse of from 12 to 30 minutes thereafter while the precipitate from the NaOH solutions is immediate and persistent. The color of the solutions in Table V is also somewhat deeper. The report that the best iron liquor to be employed for tanning is that which possesses a basicity corresponding to the formula $Fe(OH)SO_4$ is not borne out by this study or by the tanning experiments.

There are other evidences that independently show that $Fe(OH)SO_4$, or a basic ferric sulphate corresponding to this basicity, is very unstable and rapidly yields a precipitate from its solution. For instance, when a ferrous sulphate solution is oxidized by hydrogen peroxide without the addition of any acid, a precipitate is soon formed in the solution. This basic ferric sulphate is formed by the following reaction:

$$2FeSO_4 + H_2O_2 \rightarrow 2Fe(OH)SO_4.$$

Other neutral oxidizing agents, such as $KBrO_3$, that can effect this oxidation without the addition of an acid to the neutral ferrous sulphate solution, produce similar precipitates in the resulting ferric salt solution.

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TABLE V.—25 cc. SOLUTION CONTAINING 10.26 G. $Fe_2(SO_4)_3$ PER 100 CC. WITH ADDITION OF A CALCULATED AMOUNT OF NaOH SOLUTION AND DILUTION TO A TOTAL VOLUME OF 65 CC.

No.	Cc. NaOH added N = 0.4923 Trd. M. O. N = 0.4880 Trd. Phenolphthalein	Cc. H_2O added to make 65 cc.	Basicity ratio $\frac{\text{Equiv. } Fe^{+++}}{\text{Equiv. } SO_4^{=}}$	Color of solution after addition NaOH	Appearance after 30 hours' standing
1	0.00	40.00	1	(Straw yellow from start)	Straw yellow solution
2	2.70	37.30	29/28	Yellow	Reddish yellow solution
3	5.22	34.78	15/14	Reddish yellow	Light wine red solution
4	8.70	31.30	9/8	Red	Red solution
5	11.11	28.82	7/6	Deep red	Deep red solution
6	13.04	26.96	6/5	Deep red cloudy sol.	Deep red solution (Slightly turbid)
7	15.66	24.34	5/4	Deep red cloudy sol.	Deep red turbid sol. with some yellow ppt.
8	19.56	20.44	4/3	Deep red turbid sol.	Deep red turbid sol. with yellow ppt.
9	26.09	13.91	3/2	Dark red suspension	Yellow-red turbid sol. with yellow ppt. 1/6 of total volume
10	31.30	8.70	5/3	Dark red suspension	Yellow-red turbid sol. with yellow ppt. 1/5 of total volume
11	39.11	0.89	2	Black red suspension	Yellow clear super. sol. with yellow ppt. 1/3 of total volume
12	47.00	——*	5/2	Black red suspension	Straw yellow clear super. sol. with yellow ppt. 1/2 of total volume

* The total volume of this solution is 71.30 instead of 65 cc.

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In the case of ferric chloride solution, the difference is astonishing. A similar series of the ferric chloride solution was studied using Na_2CO_3 solution. The results are tabulated in Table VI. It is remarkable that throughout the whole series studied no precipitate was formed after one week's standing even where the basicity ratio was higher than the highest in the sulphate series studied above. This shows indeed that the ferric chloride is far more stable in a basic solution than the corresponding sulphate. After two weeks' standing, however, precipitate began to appear in solutions Nos. 3, 4, 5, and 6. It is interesting to note that here as in the sulphate series above (Tables IV and V) the precipitate separated out more readily from solutions of lower basicity in the series (Nos. 3, 4, 5, and 6) than form those at the end having high basicities, such as Nos. 10, 11, or 12.

The "acidity" determination, according to the method of Thomas and Baldwin[27] for the solutions of various basicity in the series studied above, can not be made in the case of the ferric salt solution, because it is found that ferric iron is rapidly reduced by the hydrogen in the presence of the platinum electrode, and no reading can be obtained.

The determination of the hydrogen ion concentration ("acidity") in iron tan liquor by a study of the rate of hydrolysis of sucrose has also a similar difficulty as one of the products of hydrolysis (glucose) has a reducing action on the ferric iron in the hot solution.

Section VI. Behavior of the Pelt Towards Iron Tan Liquor.

In view of the report[28] that iron tan liquor has the same acidity at the end of the tanning operation as it had at the beginning and also of a proposed process of iron tannage[29] using the iron tan liquor over and over again in a cycle without mentioning the necessity of readjusting the acidity of the liquor it was thought advisable to study this matter. Pickled sheepskin was cut into rectangular pieces of about 4 inches by 5 inches. These pieces

[27] "The Acidity of Chrome Liquors," by A. W. Thomas and M. E. Baldwin, This Jour., May, 1918, p. 192.

[28] "Notes sur le Tannage aux Sels de Fer," by V. Casaburi, *Le Cuir*, August 1, 1919.

[29] Bystron and Vietinghoff's Patent (German Pats. Nos. 255,320 et seq.).

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TABLE VI.—25 cc. Ferric Chloride Solution Containing 0.03228 Equiv. Fe^{+++} and 0.03042 Equiv. Cl^- with Addition of a Calculated Amount of N/2 Na_2CO_3, and Dilution to a Total Volume of 65 cc.

No.	Cc. Na_2CO_3 added N = 0.5000	Cc. H_2O added to make 65 cc.	Basicity ratio $\frac{\text{Equiv. } Fe^{+++}}{\text{Equiv. } Cl^-}$	Color of solution obtained	Appearance after 2 week's standing	Appearance after 15 week's standing
1	——	40.00	$\frac{.03238}{.03042} = 1.064$	Light yellow	Clear	Clear, no ppt.
2	0.40	39.60	15/14	Yellow	Clear	Ppt. at bottom
3	3.28	36.72	9/8	Reddish yellow	Turbid with ppt. of yellow oxide	Ppt. at bottom
4	5.34	34.66	7/6	Yellow-red	Turbid	Ppt. at bottom
5	6.88	33.12	6/5	Red	Cloudy	Cloudy, no ppt.
6	9.04	30.96	5/4	Red	Cloudy	Cloudy, no ppt.
7	12.28	27.72	4/3	Deep red	Slightly cloudy	Slightly cloudy, no ppt.
8	17.68	22.32	3/2	Dark red	Clear	Clear, no ppt.
9	21.98	18.02	5/3	Dark red	Clear	Clear, no ppt.
10	28.46	11.54	2	Very dark red	Clear	Clear, no ppt.
11	34.96	5.04	5/2	Very dark red	Clear	Clear, no ppt.
12	47.88	——*	5	Black-red	Clear	Clear, no ppt.

* The total volume of this solution is 72.88 cc. instead of 65.00 cc.

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were placed in tepid water for a short time and, when softened, introduced into cold water containing a small amount of salt to prevent plumping. The skin was then carefully neutralized with Na_2CO_3 until all mineral acid was removed, using methyl orange as an indicator. The skin was rinsed off and the excess water squeezed out so that it was roughly in the same condition as pickled skins that have been horsed up over night. The reason for neutralizing the skin in our experiments was to avoid introducing into the tan liquor an indefinite amount of the mineral acid present in the pickled skin. The tan liquor used in these experiments was a basic ferric sulphate or chloride solution, having in general a basicity of 3 equivalents of mineral acid radical to 4 equivalents of Fe^{+++} and containing iron from 11½ to 16½ g. Fe_2O_3 per liter. The volume of the tan liquor in cc. equaled from 3 to 4 times the weight in grams of the skin with excess water pressed out. Tanning was carried out in a glass jar of 1⅛ liters capacity set in a bottle shaker making about 35 R. P. M. The actual weight of the skin in these experiments was from 150 to 200 grams, and the total volume of the tan liquor 600 cc. The amount of iron used (calculated as Fe_2O_3, therefore, varied from 4.0 to 6.0 per cent. of the weight of the pelt in the thoroughly drained condition. Both Na_2CO_3 and NaOH were employed to bring about the proper basicity in the liquor for tanning. In the case of Na_2CO_3, CO_2 gas continued to be given off during tanning.

The detailed procedure was as follows. A desired amount of the stock ferric solution of known concentration and acidity was taken, and a calculated quantity of NaOH or Na_2CO_3 solution of known strength added in order to obtain the desired basicity for tanning. The solution was then diluted according to the above volume relation. The skin was immediately placed in the liquor and the container shaken in the bottle shaker. 5 cc. samples were taken for analysis at an interval of 15 minutes or longer. Iron was determined by the Zimmermann-Reinhardt method and the acidity (H_2SO_4 or HCl) by NaOH titration using 1 cc. ½ per cent. phenolphthalein solution as an indicator.* The acid deter-

* Mineral acid and iron can be determined in the same sample by first titrating with NaOH solution in the hot, allowing ferric hydroxide to collect at the bottom, filtering off the precipitate, dissolving it from the filter with a hot, dilute HCl, and then determining the iron in solution by the Zimmermann-Reinhardt method.

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mination was obtained by titration with N/10 NaOH first in the cold; and after the end-point has been reached, the solution was brought to just below boiling and titration continued until the end point was again reached. The difference between the cold and the hot end-points was only 0.15 to 0.35 cc. N/10 NaOH for a total burette reading of 10—30 cc. Four independent experiments were carried out in the case of the ferric sulphate liquor, but one set of data and results from one of these experiments will be given here which may be considered as typical.

FERRIC SULPHATE TAN LIQUOR.

Data:

Sheepskin (with excess water pressed out)..... 167 g.

Ferric sulphate liquor—

(a) Volume for tanning..... 600 cc.

(b) Concentration (calculated as Fe_2O_3).... 16.33 g. per l.

(c) Ratio of $\frac{(SO_4^{=}\ \text{Equiv.})}{(Fe^{+++}\ \text{Equiv.})}$ 0.742

Salt (about 5½ per cent.)..... 9 g.

The results are tabulated in Table VII. The skin at the end of each experiment was well tanned save for the neutralization operation which would be required in actual practice.

TABLE VII.—BEHAVIOR OF NEUTRAL PELT TOWARDS BASIC FERRIC SULPHATE LIQUOR.

		H_2^+ $SO_4^{=}$		Fe^{+++}		
Sample No.	Time interval between which samples were taken	Cc. NaOH in the hot N = 0.1096	Equiv. H_2SO_4 per l.	Cc. $KMnO_4$ N= 0.1004	Equiv. iron per l.	Ratio of Equiv. of $SO_4^{=}$ to Fe^{+++}
1*	———	20.72	0.455	10.17	0.613	742 : 1000
2	15 min.	17.88	0.392	8.63	0.520	754 : 1000
3	15 min.	16.80	0.368	7.51	0.452	815 : 1000
4	15 min.	16.13	0.354	7.21	0.435	814 : 1000
5	15 min.	15.86	0.348	6.80	0.410	849 : 1000
6	15 min.	15.54	0.341	6.61	0.398	858: 1000
7	15 min.	15.30	0.336	6.45	0.388	866 : 1000
8	15 min.	15.15	0.332	6.38	0.385	862 : 1000
9	15 min.	15.10	0.331	6.34	0.382	867 : 1000
10	30 min.	14.87	0.326	6.28	0.378	862 : 1000
11	24 hrs. Continuous shaking	14.51	0.318	6.17	0.372	855 : 1000

*NOTE.—The sample of this basic ferric sulphate tan liquor yielded a precipitate on standing, but after the skin was placed in it and tanned, all subsequent samples no longer yielded any precipitate. During tanning, the color of the liquor became lighter—from deep red to yellow—and the skin, on the other hand, was gradually colored red.

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An additional experiment was carried out using a ferric chloride liquor in place of the ferric sulphate liquor used above. In the following are tabulated the data of this experiment.

FERRIC CHLORIDE TAN LIQUOR.

Data:

Sheepskin (with excess water pressed out).....	152 g.
Ferric chloride liquor—	
(a) Volume for tanning.....	600 cc.
(b) Concentration (calculated as Fe_2O_3)....	11.60 g. per l.
(c) Ratio of $\frac{(Cl^-\ \text{Equiv.})}{(Fe^{+++}\ \text{Equiv.})}$	0.765
Salt (about 5 per cent.).....	8 g.

The results are tabulated in Table VIII. As in the case of the experiments using ferric sulphate liquor the skin was also well tanned in the ferric chloride liquor and no neutralization was effected.

TABLE VIII.—BEHAVIOR OF NEUTRAL PELT TOWARDS BASIC FERRIC CHLORIDE LIQUOR.

Sample No.	Time interval between which samples were taken	HCl: Cc. NaOH in the hot N = 0.1104	HCl: Equiv. HCl per l.	Fe^{+++}: Cc. $KMnO_4$ N = 0.1087	Fe^{+++}: Equiv. iron per l.	Ratio of Equiv. of Cl^- to Fe^{+++}
1*	———	15.00	0.333	6.66	0.435	765 : 1000
2	15 min.	13.16	0.291	5.74	0.374	778 : 1000
3	15 min.	12.44	0.275	5.31	0.346	795 : 1000
4	15 min.	12.07	0.267	5.07	0.331	806 : 1000
5	15 min.	11.95	0.264	4.76	0.311	849 : 1000
6	15 min.	11.90	0.263	4.63	0.302	871 : 1000
7	15 min.	11.89	0.263	4.59	0.300	876 : 1000
8	15 min.	11.82	0.261	4.61	0.301	868 : 1000
9	15 min.	11.80	0.261	4.51	0.294	887 : 1000
10	24 hrs. Continuous shaking	11.70	0.259	4.47	0.292	887 : 1000

*NOTE.—None of these samples (including sample No. 1) of this basic ferric chloride liquor yielded any precipitate on standing. The colors of these samples were decreased from deep red (sample No. 1) to light yellow (sample No. 10). On the other hand, the red color of the skins became deepened as the tanning operation progressed.

From these results the following important conclusions can be drawn:

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(1) Iron is taken up by the skin very rapidly at the beginning of the tanning operation, and from 30 to 40 per cent. of the total is taken up by the pelt before neutralization.

(2) The mineral acid (sulphuric acid or hydrochloric acid) is also taken up by the skin in a similar manner, the total amount absorbed by the neutral pelt being in general about 20 to 30 per cent. of the total. (If pickled skins are not neutralized before tanning as in actual practice, a correspondingly less amount of the acid will be taken up by the skin. That the skin absorbs the sulphuric or hydrochloric acid from the liquor is corroborated in actual tanning practice by the fact that only 70—80 per cent. of the theoretical amount of alkali is required to effect the complete neutralization. See later Section on Pure Iron Tannage.)

(3) Although the mineral acid is also taken up by the pelt, it is not taken up in the same proportion as the iron so that the liquor is more acid towards the end of the tanning operation than at the beginning.

(4) The curves of absorption of both the iron and the acid by the pelt with respect to the time of tanning approach some constant horizontal lines asymptotically.

(5) The tanning reaction is practically completed within one and a half hours of drumming and the neutralization operation can begin after 1¼ to 1½ hours of drumming, it being neither necessary nor advisable to allow the pelt to remain in the liquor for longer than 1½ hours before neutralization takes place.

(6) Both the basic ferric sulphate liquor and the basic ferric chloride liquor behave alike towards the pelt, the only difference being that the ferric chloride liquor possesses decidedly less tendency to yield the precipitate of hydrated ferric oxide than does the ferric sulphate liquor.

Although burette readings for NaOH are expressed in four significant figures, the precision for the results obtained in many cases is probably not much better than 1 per cent. For, in the first place, the samples taken for analysis are small (only 5 cc.) and, in the second place, the organic particles, such as fatty matters, skin fibers, etc., present in the tan liquor make accurate sampling rather difficult. Furthermore, the presence of grease causes tiny drops of the liquor to adhere to the walls of the pipette, so that frequent cleaning by means of a cleaning solution

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FIG. — III

Curves Showing Absorption of Fe and H_2SO_4 during Tanning

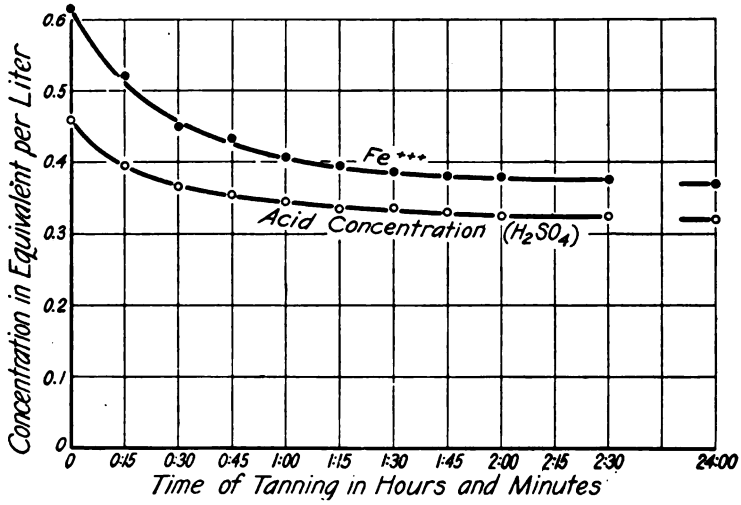
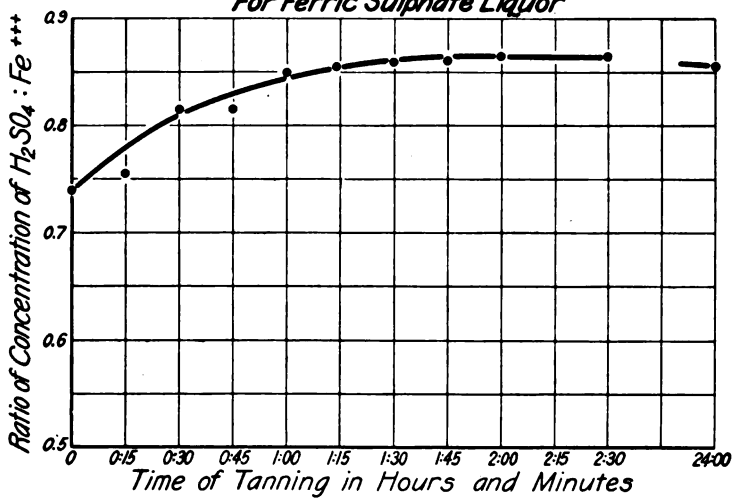


FIG. — IV

Curve Showing Increase in Acid Concentration during Tanning For Ferric Sulphate Liquor



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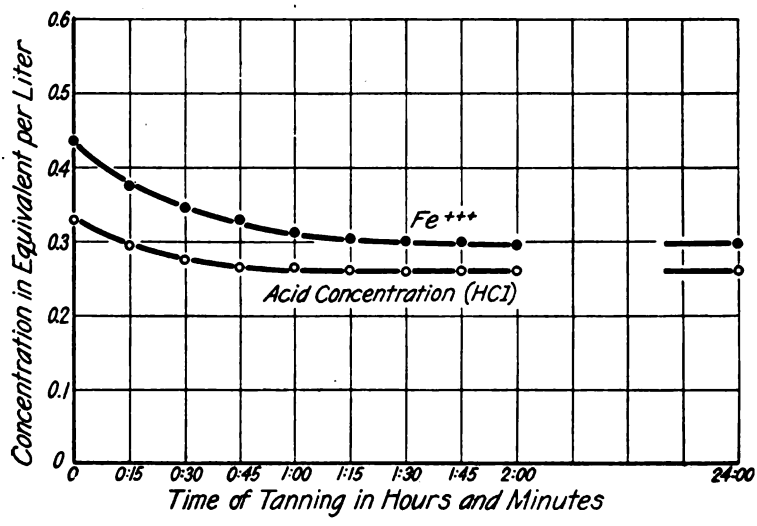
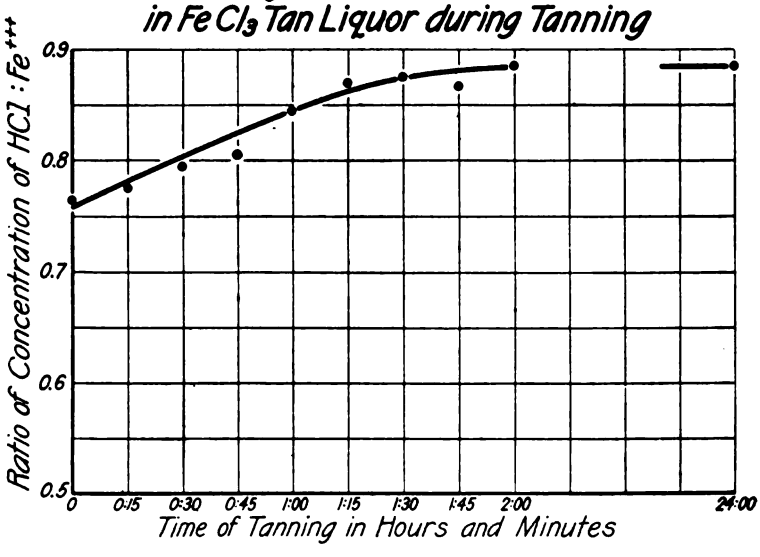
FIG—V

Curves Showing Absorption of Fe and HCl during Tanning



FIG—VI

Curve Showing Increase in Acid Concentration in $FeCl_3$ Tan Liquor during Tanning



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is necessary. Considerable difficulty is also experienced due to the fact that the presence of the organic matter in the liquor interferes with the determination of iron by the $KMnO_4$ titration. This difficulty is finally overcome by oxidizing all the organic matter present in the sample with $KMnO_4$ in the presence of HCl until a purple color is seen. The sample is then heated, reduced with $SnCl_2$, and titrated with $KMnO_4$ solution in the usual manner.

It was observed in tanning experiments using a wooden drum that a completely oxidized iron tan liquor gave a copious precipitate when tested with $K_3Fe(CN)_6$ solution at the end of the tanning operation. Evidently the tan liquor is subject to reduction by the skin, the woody material and the metallic parts of the drum, and organic impurities that may collect in the drum. The amount of reduction in the tan liquor by the skin alone has been determined. For such purpose, the skin was tanned in a glass container with a completely oxidized ferric sulphate liquor. The skin was allowed to remain in the liquor with continuous shaking for 24 hours. In this particular experiment, an amount of iron containing 14½ per cent. $Fe_2(SO_4)_3$ of the weight of the drained skin, dissolved in water equal to 3½ times the weight of the skin, was used. Ferric iron in the sample taken at the end of 24 hours was determined by means of a titanous sulphate, $Ti_2(SO_4)_3$ in H_2SO_4 solution using ½ cc. normal NH_4CNS solution as an indicator, while total iron was determined by $KMnO_4$ titration after oxidizing off all the organic impurities in the sample with $KMnO_4$. It was found that 4.4 per cent. of the total iron in the liquor had been reduced to the ferrous state. This amount of reduction was exclusively due to the skin. In actual practice where a wooden drum is used with whatever dirt that may collect in it, the percentage of the iron reduced must be greater.

Section VII. Experiments on Tanning With Ferric Hydroxide Hydrosol.

A ferric hydroxide hydrosol was prepared and applied to tanning for two reasons: (1) that it was desired to study the tanning action of ferric iron completely in the colloid state, and (2) that as a sol requires for its stability only the small amount of an

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electrolyte that is retained with the colloid,* the tan liquor can be considered to be practically free from an electrolyte and consequently the function of a neutral electrolyte such as NaCl, Na_2SO_4, etc., used in a mineral tanning liquor will thereby be disclosed. The sol was made by the peptization method. For such a purpose a fairly concentrated (about 30 per cent.) ferric chloride solution was taken and a dilute ammonia solution (1 vol. 0.90 NH_4OH to 8 or 10 vol. water) added drop by drop, while the solution was stirred by a mechanical stirrer. On adding NH_4OH the yellow-red solution turned brown and finally almost black by reflected light. The addition of NH_3 was continued until solid particles of ferric hydroxide were re-dissolved only after 5 to 10 minutes continuous stirring. The sol was dialyzed in collodion sacks first in running tap water over night and then in distilled water for 6 days, changing the distilled water three times every 24 hours. The sol thus obtained was rather diluted as much water had entered the sacks during dialysis by virtue of the osmotic pressure, and it was necessary to concentrate it by evaporation. After concentration it was filtered through cotton.

This sol was coagulated by an electrolyte such as NaCl when a certain concentration of it was reached. On standing the coagulated ferric hydroxide settled at the bottom, leaving the supernatant solution colorless. When it was coagulated by HCl, added in some excess, however, the precipitate, on standing, re-dissolved giving a yellow solution of ferric chloride. A dilute sol prepared as above but dialyzed for seven days showed a misty beam of light under an ultramicroscope. The particles are so small that they can not be counted and their motions are not discernible although a distinct mist is seen. The electrical charge of the sol was determined by cataphoresis. This was determined in the ordinary U-tubes using KCl solution of the same conductivity as the sol in the upper portions of each branch in which the electrode was immersed. The sol moved toward the negative electrode, showing it to be positively charged, as would have been expected.

The tanning action of the sol toward a carefully neutralized, nearly salt-free sheepskin was studied. For this purpose, a piece of pickled sheepskin (4¾ in. x 8¾ in.) was first softened in water in the presence of a small amount of salt. It was carefully

* The "Complex" Theory of Colloids.

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neutralized with Na_2CO_3 solution using methyl orange as an indicator, and the salt was washed out from the skin as far as possible (without causing undue plumping) when only a small amount of AgCl was formed in the wash water tested with an $AgNO_3$ solution. The excess water was pressed out from the skin and its weight in this condition was 51 g. A 250 cc. portion of the ferric hydroxide hydrosol (analysis giving 0.963 g. Fe_2O_3 per 100 cc.) was taken and the neutralized, nearly salt-free skin shaken in it continuously for 2½ hours. The sol was not coagulated but the skin swelled to about three times its original thickness, becoming stiff and rubber-like. It was not tanned. Five per cent. salt (2.5 g.) was next added and the shaking continued for one hour longer. The skin had fallen but was not tanned and the inner layer was not even penetrated. The sol was coagulated by the addition of the sodium chloride.

The experiment was repeated in exactly the same manner, using, however, a well pickled skin instead of the de-pickled and salt-free skin. No salt was added. The hydrosol was again coagulated by the small amount of the H_2SO_4 and NaCl left in the pickled skin, yet the skin swelled badly. The cross section of the skin showed red lines on the outside edges and a large white untanned band in between.

From this it appears that the presence of an electrolyte such as NaCl or Na_2SO_4 in the tan liquor is to prevent plumping so that the pelt is kept "fallen" in the liquor so as to be readily penetrated by the tanning agent. It must be observed that the plumping of the pelt in the hydrosol is not caused by the acid liberated during tanning, for there is only a negligible amount of an acid radical that can be retained in the sol, but by simple inhibition of water by the gelatine material of the pelt in this neutral sol. It appears also that ferric hydroxide in a pure sol form can not be employed for tanning purposes; for without a sufficient amount of an electrolyte, the pelt would be caused to swell and not be penetrated; but if sufficient electrolyte is added to prevent plumping, the sol is coagulated at once to a gel which likewise would not penetrate the pelt. It is evident that a pure iron sol will not act as a tanning agent; hence the theory of leather formation by colloidal co-precipitation alone is open to doubt, and the reaction may be purely chemical.

[*To be Continued*]

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ABSTRACTS.

The Sweating Process of De-Wooling. *Bulletin of the Bureau of Bio-Technology* through *Lea. Tr. Rev.*, **54**, 110 (1921). The process of sweating is probably one of the oldest industrial methods still in use. Wool removed by sweating has the greatest value to the textile manufacture and this process is unquestionably the cheaper. If the abnormal loss of hide substance which occurs in sweating were avoided the principle disadvantage of this method would be eliminated. This investigation was undertaken as an endeavor to establish a further means of control of this process. The form of damage known as "run" pelt received first attention. The damage occurs as circular or oval pitted markings, found after sweating, usually upon the flesh side but also frequently on the grain. Examination of the pitted skins revealed the presence of a species of nematode and experiments appeared to prove that this organism is responsible for the localized breaking down of the hide substance which results in pitting. They may be found in all putrefying material and were isolated from decaying vegetables, rotten wood, dung and limed hair from sole leather tannery. They are found in large numbers upon all run pelts, whilst on undamaged pelts, if found at all, they are exceedingly few in number; although no living forms were found in the soaking pits, a portion of wood from the ranges in a sweating room was found to be covered with organic matter containing the worms, which lived for two or three weeks without further nutriment. This species does not withstand desiccation and were not found on dried skins.

The nematoda require their nutriment to be in the form of organic juices. They possess tooth like appendages, but these are for boring and disintegrating rather than for mastication. They are doubtless largely dependent on liquefactive bacteria for the reduction of the material to a partially digested state, but it is also suggested that they may secrete a proteolytic enzyme themselves.

The conclusions arrived at are that the worms are not present in the skins when they are received at the fellmongery, but that they are actually being cultivated in the sweating chambers under optimum conditions. Cleanliness seems to be at least a partial remedy for this form of damage. Further investigations are in progress.

Skin Structure and Bating. By A. Seymour-Jones, *J. S. L. T. C.*, **4**, 291 (1920). The elastic fibers act as ties or supports to maintain the erect position of the white collagenous fibers. They are responsible for holding the structural scheme of the grain together and for creating the necessary elastic cushion of the skin. The elastic fibers are digested by trypsin, consequently the supports of the entire grain membrane are removed, and the grain membrane and grain layer collapse, *i. e.*, become flaccid. Thus the principle object of bating is accomplished.

The author recommends that bating be accomplished in three operations; namely, (1) deliming by means of an acid, (2) reduction of the

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grain membrane and grain by the use of trypsin, (3) removal of fat, in the pelt state, from the fatty layer.

Chrome Leather Analysis. REPORT NO. 2 OF SUB-COMMITTEE. By R. F. INNES, *J. S. L. T. C.*, **4**, 294 (1920). The committee made the following determinations on four classes of leather:—Moisture, free sulphur, water solubles, total alkali expressed as Na_2SO_4, basicity of the chromium salt on the fiber, chromium soluble in petroleum ether as Cr_2O_3, soluble ash, total petroleum ether extract, total ash and total Cr_2O_3. The four leathers were:—glace kid fat-liquored with soap and oil; box side fat-liquored with pure sulphonated cod oil; dull chrome side fat-liquored with soap, cod oil, and degras; and chrome sheep. The committee confirmed the results of the chairman that petroleum ether extracts as much sulphur from chrome leather as carbon bisulphide. Two methods used for water solubles did not prove satisfactory. The committee also considered the estimation of soap in a fat-liquored chrome leather. No soap could be found in the water extract of either of the leathers examined. The chairman's contribution on this point is given in an appendix to the report and his conclusions were as follows:—In soap fat-liquoring of a chromed goat skin an acid chrome soap is formed which is not wholly extracted by petroleum ether. This is formed by double decomposition of the soap with the basic chromium sulphate with liberation of potassium sulphate which to a great extent remains in the solution. It seems that soap cannot be estimated in a fat-liquored skin by extraction with water since the soap is no longer soluble in water. It also follows that a sodium or potassium soap containing the same proportion and same kind of fatty acids would give the same kind of leather, the alkali in both cases being to a great extent a carrier only of the fatty acids. This was confirmed by fat-liquoring two batches of leather under the same conditions with a hard soap and a soft soap. No difference could be detected and also no potassium was found in that treated with the potash soap.

The Extraction of Grease from Leather. DRESSING LEATHER SUB-COMMITTEE. *J. S. L. T. C.*, **4**, 300 (1920). The committee has continued its investigation of the extraction of grease from leather. The four leathers used were stuffed as follows:—(1) Fat-liquored with a solution of soft soap only, (2) fat-liquored with a mixture of castor oil and soft soap, (3) fat-liquored with sulphonated castor oil, (4) fat-liquored with oleic acid and soft soap. The committee recommended that either chloroform or benzene be officially recognized as the solvent to be used in all determinations of grease in leather. If weight is to be attached to the color of the extract, then benzene shows to greater advantage than chloroform as the latter always gives a dark colored extract.

A Difficulty in Dyeing Wool. By PASCAL HUC, *Les Industries du Cuir*, 1920, 333. A sample of white wool, perfectly degreased, when dyed acid black showed dirty yellow stains. A chemical and microscopical

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examination revealed no difference from ordinary wool, neither could any adulterant, *e. g.*, baryta, kaolin, or stearic acid, be detected. The trouble was traced to too rapid sweating, causing the wool in part to be transformed to lanuginic acid, thus diminishing the basicity of the fiber and in parts rendering its impermeable. By means of suitable mordanting the trouble was overcome. *J. S. L. T. C.*

Ropiness in Wattle Bark Infusions. By R. G. SMITH, *Proc. Lin. Soc.* (N. S. W.), 1920, p. 52; *Chem. Abstr.*, 1920, p. 3,166. Ropiness is due to bacteria, two types of which have been isolated. The "disease" can only take place in very weak liquors and in a 2 per cent. tannin solution; ropiness was prevented owing to the tannin coagulating the slime upon the bacteria. Acidity and a number of sugars (but not all) favor the growth, which can be prevented by adding 3 pounds of sodium acetate per 1,000 gallons of water. The substance formed is a glactan and is hydrolyzed by H_2SO_4 to galactose. *J. S. L. T. C.*

Researches on the Processes of Tanning—II. By W. MOELLER, *Ledertech. Rund.*, **12**, 177 and 189 (1920). Hide powders obtained from the work reported on in the first communication, after treatment with three different concentrations each of phenol, tannic acid and quebracho for a period of three months, were washed with cold water and the amount of material and hide substance washed out were determined. To each hide powder 100 cc. of water was added and the mixture allowed to stand one day, the solution filtered off, measured and tested. Enough water added to the hide powder again to make 100 cc. and allowed to stand eight days, after removing the aqueous solution this washing procedure was repeated twice again. The third washing was allowed to stand 14 days and the fourth 1 month. The amount of phenol removed by the first washing from the hide powder treated with phenol is very large, that by the second washing is very low and the third yields practically none, while the fourth does not give even a trace. Although the total quantity of phenol removed by all of the washings, in no case exceeds 79 per cent. of the amount taken up by the hide powder it is considered that all of the phenol is removed by washing with water and that the difference is due to loss of phenol by evaporation and to imperfections in the method of determining it. The amount of hide substance removed by the first three washings is normal, but the fourth washing shows a very great increase in soluble hide substance which the author considers as an indication that all of the phenol has been removed. In the case of hide powder treated with tannic acid a noteworthy difference is shown. That treated with the 1 per cent. solution gave up practically nothing to the distilled water for the first two washings (1 day and 8 days). The migration of the tannin begins to increase after this and for the 14-day period it amounts to 5 per cent. and for the 1-month period to 12.5 per cent. The total removed from the powder in the four washings equalled about 20 per cent. That treated with the 3.5 per cent. solution exhibited the same general tendency toward wash-

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ing, but that treated with the 5 per cent. solution is directly opposed in its tendency toward the others; that is, the largest quantity (20 per cent.) is removed by the first washing and that of the succeeding washings decreases, the fourth washing removing 1.8 per cent., a total of 52 per cent. being removed by the four washings. The amount of hide substance removed by the first and second washing remains normal, increases considerably in the third and fourth washing for the powders treated with the 1 and 3½ per cent. solutions and only a little with the 5 per cent. solution. The total amount of hide substance removed in the washings decreases with increasing concentration. These results with tannic acid solutions the author considers a confirmation of his assumption that tannic acid is not a complete tanning system, but contains an excess of phenolic bodies which act as peptizers and which are reversibly adsorbed, hence easily washed out. The hide powders treated with quebracho solutions act in the same general manner as that treated with the 5 per cent. solution of tannic acid when subjected to washing as outlined. The first washing removed 50 per cent. and more of the total washed out and there is a decrease in the residue of each succeeding washing until after the fourth (1 month) when only traces are found. The total washed out of these hide powders in four washings is 41 per cent. for that treated with the 1 per cent. solution, 15 per cent. for the 3.5 per cent. solution and 17 per cent. for the 5 per cent. solution. The amount of hide substance dissolved in these experiments with quebracho remains normal throughout with the exception of a slight increase in the last two washings for the powder treated with the 1 per cent. solution. This is taken to indicate that true leather substance has been formed with quebracho and that as soon as the peptizers of phenolic character are removed from the leather the washing out of tanning material comes to a standstill.

Leather is defined as animal hide whose elementary parts are protected from hydrolytic and fermentative influences by submicroscopic crystals of the particles of tanning material. This definition is a modern conception of the "coating" theory. Knapp thought that the whole fiber was coated with the tanning material, but it has been demonstrated in more recent times that the fiber is composed of innumerable submicroscopic fibrils and these fibrils of still smaller divisions. The author claims that tanning consists of coating the micells with submicroscopic crystals of tanning materials and hence is beyond the power of being detected by the ordinary microscope, but can be detected with the ultramicroscope. This explanation removes the principal argument of advocates of the chemical theory against the coating theory as all have used the microscope to attempt to disprove it. G. W. S.

Researches on the Processes of Tanning—III. By W. Moeller, *Ledertech. Rund.*, **13**, 1 and 10 (1921). The experiments given in the first communication (abst. This Jour., **16**, 166 (1921)) were continued under other conditions. Experiments were made using volumes of 100 cc. but of much greater concentration, and with volumes of 1,000 cc. of approximately the

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same concentrations. The same amount of hide powder being used in all cases. The experiments with phenol using a tenfold larger volume gave the same general results as those with the small volume. The experiments with large volumes of tannic acid solutions showed that for a period of action of 1 day the hide powder absorbed more tannin from the dilute solution and less from the concentrated and the same was true for the 8-day period with a slight increase in the amounts absorbed. For the 14-day, 1-month and 3-month periods the amounts absorbed followed the adsorption law—there was less absorbed from the dilute solution and more from the concentrated. With increase in time of the reaction there is a decrease in the amount absorbed from the dilute solution, a slight decrease in the amount absorbed from the mean solution and a gradual increase in the amount absorbed from the strong solution. The amount of hide substance removed in solution was greatest for the dilute solution and least for the strong solution and remained approximately the same for the different time periods. The results with 100 cc. of tannic acid solutions of approximately 10, 20 and 30 per cent. strengths showed that for a 1-day period the hide powder absorbs most from the 20 per cent. and least from the 30 per cent. solution; for the 1-month period most from the 10 per cent. and least from the 20 per cent. solution; and for the 3-month period most from the 20 per cent. and least from the 10 per cent. solution. There was an increase in the amount absorbed from each solution with increase in time with no indication that equilibrium obtained at the end of 3 months. The amount of hide substance removed in solution is greatest for the 30 per cent. and least for the 10 per cent. solution with practically no change due to time. With the large volume of quebracho solutions it was found that least was taken up by the hide powder from the 1 per cent. solution and most from the 6 per cent. solution for all periods of time. There was an increase in the amount absorbed from each concentration with increase of time with every indication that the absorption would continue after 3 months. The experiments with 100 cc. of concentrated solutions of quebracho gave results similar to those with concentrated tannic acid solution with the exception that there was a slight increase in the amount absorbed up to a maximum for a period of time of 1 month after which there was a decrease. This is a confirmation of the law established by von Schroeder and Paessler that the greatest absorption occurs up to a certain concentration of the solution beyond which there is no further increase or a slight decrease. The author claims that his explanation of these phenomena set forth in the first communication (*l. c.*) is verified by these results. The reason the absorption of quebracho from concentrated solutions comes to a standstill is that the quebracho tanning material predominantly consists of peptized material and that therefore there is no great excess of peptizer to re-peptize the precipitated material as is the case with tannic acid, hence an increase in absorption cannot take place upon prolonging the time of action. Not only is the peptization equilibrium and degree of dispersion dependent on the concentration, but they are also influenced to a great extent by temperature.

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These experiments were carried out at a temperature of 18° C. when the 6 per cent. solution was in the most favorable condition, reaching the adsorption value of about 138 per cent. of the dry weight of hide powder used. The most unfavorable was the 30 per cent. solution. With increase of temperature the concentration could be raised and the best results still be obtained, practical drum tanning with concentrated quebracho solutions is explained by this fact. G. W. S.

PATENTS.

Process and Apparatus for the Instantaneous Tannage of Hides and Skins. U. S. Patent 1,363,771. F. GILARDINI, Turin, Italy. Filed Apr. 6, 1918. Method of tanning hides which comprises protecting portions of the hide and simultaneously tanning the unprotected portions thereof, exposing the previously protected portions and tanning the same.

Process for Making Leather with the Assistance of Iron Salts. U. S. Patent 1,364,316. O. RÖHM, Darmstadt, Germany. Filed Mar. 10, 1917. The process for producing leather which consists in subjecting the skins to the action of aldehydes and ferric iron salts.

Process for Producing Leather with the Assistance of Iron Salts. U. S. Patent 1,364,317. O. RÖHM, Darmstadt, Germany. Filed Mar. 10, 1917. The process for producing leather which consists in tanning the skins with basic ferric iron chloride followed by a neutralization with ferric iron compound precipitating substances and a treatment with aldehydes.

Tanning Apparatus. U. S. Patent 1,364,379. A. S. JONES, Redwood City, Cal. Filed April 22, 1919. A tanning vat, a carriage, means for reciprocating the carriage horizontally, means for suspending from said carriage sheets of material, and an obstruction in the vat against which said sheets impinge and fold upon as they reciprocate in a horizontal direction therein.

Leather-Finishing Machine. U. S. Patent 1,365,389. W. E. FEIGE, Milford, Mass. Filed Feb. 26, 1920.

Apparatus for Treating Leather or Other Goods. U. S. Patent 1,365,573. W. J. WALKER, Warrington, England. Filed Dec. 15, 1919. An agitating mechanism for soaking or similarly treating hides, skins, leather or other goods, comprising, a vat for the liquor, a frame reciprocated vertically in the liquor and extending over a considerable area of the vat, said frame being adapted to bodily rise and fall, a series of non-return valves in said frame, said valves being adapted to open on the downward movement of the frame and close on the return movement, and means for vertically reciprocating the frame.

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Method of Treating Leather. U. S. Patent 1,369,240. S. O. HAHN, Lincoln, Nebr., assignor to The Chrome Leather and Rubber Tire Company, Inc., Pueblo, Colo. Filed Feb. 16, 1920. The method of treating leather which consists in separating from ordinary commercial rubber cement a portion of the sulphur thereof to produce a cement of a decidedly lower sulphur content than the ordinary commercial rubber cement, then forcing the residue into the body beyond the surface of the latter to impregnate the leather and subsequently vulcanizing rubber to the leather so treated whereby the rubber and leather are united into substantially an integral mass.

Tanning, Etc. British Patent 152,641. ELEKTRO-OSMOSE AKT.-GES. (GRAF SCHWERIN GES.), Berlin. Aug. 16, 1920. Material to be treated by any tanning, impregnating, or like process is submitted to a preliminary treatment consisting in subjecting it to the action of an electric current in pure water. This is stated to shorten and render more economical the subsequent process and also to have a de-liming effect. The preliminary treatment in pure water may be conducted with diaphragms or the hide, etc., may be suspended between two poles and subjected to the electric current. The subsequent treatment may comprise electro-osmotic tanning or mechanical tanning or a combination of these processes. In an example, an ox-hide de-limed with dilute formic acid is electrically treated in pure water for 10 hours, being then electro-osmotically tanned in chestnut wood extract of 2° Bé. and subsequently mechanically tanned with a similar extract of 3° Bé. In another example, after the preliminary treatment in water, bark or chrome tanned leather is impregnated or fatted by electro-osmotic treatment with dégras in soap solution for 8 hours.

Leather. British Patent 154,103. J. T. WOOD, Nottingham. Feb. 4, 1920. In puering or bating goat and other skins by means of tryptic or other enzymes, the enzyme is applied as a paste to the grain side only in order to prevent loss of substance and weight. The skin is subsequently washed and, if necessary, delimed by means of an acid bath, previous to tanning. The activity of the paste may be regulated by dilution with an inert material such as kaolin or wood-meal.

Synthetic Tanning Agents. British Patent 154,153. CHEMISCHE FABRIKEN WORMS AKT.-GES., Frankfort-on-Main, Germany. Nov. 17, 1920. An aromatic hydroxy compound or an alkali salt thereof, an aldehyde, and an acid sulphite are condensed together in solution at ordinary pressures and at temperatures up to 100° C. The phenol used may be a mixture and may be in the form of a solution of its alkali salt as obtained technically. According to examples, commercial phenol or carbolic liquor is condensed with formaldehyde or acetaldehyde, and sodium bisulphite. The products are suitable for tanning agents, with or without addition of other tanning agents or a metallic salt.

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ANNUAL MEETING.

The eighteenth annual meeting of the A. L. C. A. will be held at the Hotel Ambassador, Atlantic City, N. J., on June 9, 10 and 11, 1921.

The following schedule of rates has been received:

European plan, per day:

Single	$6, $8, $11
Double	$8, $10, $13
Triple	$10, $12, $15

American plan, $6 per person a day in addition to above rates.

Reservations should be made by communicating direct with the management of the Ambassador.

PROPOSED CHANGES IN THE OFFICIAL METHODS.

Since the more or less general adoption of the circular saw apparatus for the preparation of heavy leathers no doubt many of the laboratories have noticed that such prepared samples are very light and voluminous, and that the official charges for moisture and ash require larger apparatus than formerly. This not only means a change in apparatus but also necessitates the use, for crucibles especially, of heavier and larger ones which take up decidedly more room in the muffle and desiccators.

It is suggested that the official methods for analysis of vegetable tanned leather be changed to read as follows:

(2) *Moisture.*—Dry 5 to 10 grams of leather for 16 hours at a temperature between 95°-100° C.

(4) *Ash.*—Incinerate 5 to 15 grams of leather in a tared dish at a dull red heat until carbon is consumed. If it is difficult to burn off all the carbon, treat the ash with hot water, filter through an ashless filter, ignite filter and residue. Add the filtrate, evaporate to dryness and ignite.

If the sample is correct, these changes would appear to be of such a nature as not to require laboratory work for verification and simply could be voted into the methods. Such changes would permit the use of more convenient size apparatus, whereas at present for official work one is compelled simply from the wording of the methods to use apparatus sufficiently large to accommodate the official charge of at least 10 grams.

(Signed) R. W. FREY.

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IRON TANNAGE.

By Daniel D. Jackson and Te Pang Hou.

[*Continued from page 219*]

SECTION 8. GENERAL EXPERIMENTAL WORK ON IRON TANNING.

The requirements of a good tannage are (1) that the pelt shall be converted into a net work of isolated fibers and become no longer putrescible, and (2) that this conversion shall be irreversible, *i. e.*, the leather so obtained shall not be readily affected, or reverted to the raw condition, by water or other agency (acid-alkali treatments excepted). In addition it might be mentioned that the leather obtained shall keep well, *i. e.*, it shall not spontaneously deteriorate on storing or in use within a reasonable length of period. Iron tannage can yield a leather that will fulfill all these requirements when it is properly carried out.

In research work on this subject many difficulties have been encountered. Since no detailed data on the subject are available in the existing literature, much time has been spent in determining conditions for a successful working. A ferrous sulphate solution was employed as such and found to have no tanning property.* Oxidation of the iron was then resorted to, but the question arose as to what oxidizing agent should be employed and in what manner the oxidation should be effected. Sodium nitrite and sulphuric acid, bleaching powder and acetic acid or sulphuric acid, sodium dichromate and sulphuric acid were among the oxidizing agents first employed. The question of completeness in oxidation, the relation of acidity of ferrous sulphate solution to oxidation, and the reduction of the ferric iron in the liquor by organic materials in contact with it were matters that were gradually brought to light. The basicity of the iron liquor used for tanning exercised

* The experiment was carried out as follows:

Skin (sheepskin pickled, with water pressed out)	40	g.
Salt (5 per cent.)	2	g.
Ferrous sulphate ($FeSO_4.7H_2O$) (14 per cent.)	5.6	g.
Water (3 times the weight of skin)	120	cc.

The solution was then made slightly alkaline up to the point of the beginning of the precipitation of the green $Fe(OH)_2$. The skin was shaken in it for 1½ hours and found to remain soft and unaffected. On drying the skin so treated was practically in the same condition as a dry pickled skin with dark spots and areas of contracted grain shown on the grain side. It was affected by water and plumped in it.

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an unlooked-for influence.* For, when it was not properly adjusted, either no satisfactory tannage was obtained, or much yellow precipitate was deposited so that the pelt was difficult to tan through.

After some experimentation a tannage was found possible and the pelt was apparently well tanned while in wet condition. On drying, however, the pelt shrunk and the color of the grain was uneven. Dark wrinkled spots appeared on the grain and often the skin on drying looked horny and transparent. The leather was stiff, and the grain brittle.†

Since a comparatively high percentage of the iron salt of the weight of the pelt is needed, this necessitates the use of a small amount of water and the employment of a somewhat concentrated liquor ("short liquor") in an attempt to cut down the quantity of

* To investigate the effect of the basicity of the tan liquor on the skin (neutralized) tanned in it, four tan liquors with different degrees of basicity were prepared and the skins tanned in them. The skins, after being shaken in these liquors for 15 minutes, were examined and the results tabulated as follows:

TABLE IX.

Basicity ratio $\frac{\text{Equiv. Fe}^{+++}}{\text{Equiv. SO}_4^=}$	Color of tan liquor	Color of skin shaken for 15 min.	Character of skin after 15 min. shaking
6/5	Deep red (Clear sol.)	Reddish straw color	Skin penetrated by sol.
5/4	Dark red (Clear sol.)	Light red	Skin tanned through
4/3	Dark red (Cloudy sol.)	Red-yellow	Skin tanned through
3/2	Black red Turbid sus.	Brown-yellow	Pigment crust on surface layer Skin barely tanned through

It will be noticed that when the liquor is of the right basicity the color of the skin in contact with it should be more red than yellow.

† If, however, before the pelt (skin) was permitted to dry completely it was stretched or knee-slaked while still in a sammied condition, the brittleness of the grain on complete drying could be overcome. This amounts to separating the fibers by mechanical means rather than from the natural result of tanning. A well pickled skin could be made soft and flexible as if tanned, when worked in the same way.

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the iron salt taken.* The phenomenon of "grain drawing" is then apt to occur if the liquor is not carefully introduced and the pelt properly prepared.

Finally, after satisfactory tannage could be obtained the problem of coloring presented another phase of difficulty. The yellow-red color of the leather makes dyeing to a light color ("fancy color") impossible. Further, the iron in the leather is active so that it combines with many substances to form insoluble compounds having generally an objectionable color. Vegetable retanning is limited to cases where a gray or black leather is desired. The interference of iron with dyeing by means of basic dyes to a color other than black constitutes another difficulty on account of the chemical action of iron on many a vegetable mordant required when such dyes are to be used. On the other hand, in certain cases where chemical activity of iron is utilized for the coloring of the leather by a treatment with substances capable of producing color lakes with iron (*e. g.*, with $K_4Fe(CN)_6$ for blue coloring) the leather then becomes hard and brittle, probably due to the withdrawal of iron from the fibers for the formation of the inert color lakes. Consequently the leather is to a greater or less extent detanned.† Furthermore, the color of the leather thus produced is not fast and is slowly washed out unless this treatment is immediately followed by oiling or fat-liquoring. On the other hand, the same detanning effect also results when an attempt is made to bleach the iron tanned leather by means of a reducing agent such as bisulphite or thiosulphate followed by an acid.

Some methods that have been employed to overcome these difficulties may be mentioned. It was found that improper tannage more than anything else was responsible for the brittleness of

* Similar improvement has been successfully made in chrome tannage. Thus, from a private communication, a process of two-bath chrome tannage for skins consisting of (1) *pickling* with 3 per cent. salt, 1 per cent. 66° Bé. H_2SO_4 in 2 gallons water per 100 pounds, drumming for 20 minutes; (2) *chroming* with 3 per cent. $Na_2Cr_2O_7.2H_2O$, 1 per cent. 66° Bé. H_2SO_4 in 2 gallons water, drumming for 2 hours; and (3) *reducing* with 1½ per cent. 66° Bé. H_2SO_4 in 1 gallon water (added first) and 14½ per cent. "hypo" in 2 gallons of water, drumming for 2 hours, has been successfully employed, giving a very soft, light-colored leather.

† If the neutralized tanned pelt is first dried to "crust" and then wetted back for this treatment, the effect of detanning is less marked.

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the leather. When a pelt is not uniformly tanned through, due to either the liquor employed being too alkaline or subsequent neutralization too rapid, the outer layer (the grain) becomes dense and crusty, while the inner layer remains soft. The whole pelt on drying, therefore does not contract uniformly and the shrinking or curling up of the pelt results. This leads to the breaking of the grain on bending. When much iron in the tan liquor has been reduced to the ferrous state and found its way to the pelt, it will become oxidized during drying. This appears to be responsible for dark, wrinkled, hard spots appearing on the grain.

The solutions to some of these problems were found in the use of a completely oxidized iron tan liquor; the employment of a small excess of the oxidizing agent in the liquor; the maintenance of iron in the ferric state by means of an after oxidation; the use of optimum basicity for tanning; and the careful neutralization of the pelt after tanning. All these will be dealt with at some length in the following sections.

The ferric sulphate in solution is unstable and liable to be decomposed by hydrolysis from a neutral or slightly alkaline solution, and is very rapidly precipitated upon the introduction of an alkali. Some attention has been devoted to investigating the possibility of correcting this tendency. The use of organic protective colloids, or of gums that form mucilages in water, or of substances that chemically combine with iron to prevent precipitation of ferric hydroxide from an alkaline solution, entails many complications. The difficulties in such cases are (1) that those nitrogenous protective colloids such as gelatine, egg albumin, blood albumin, etc., that are extensively used in connection with the other parts of leather manufacture are themselves coagulated by the highly concentrated tan liquor; (2) that the poly-hydroxy alcohols* in the form of syrup glucose, gum dextrin, starch, etc., exert a more or less reducing action on the ferric iron in the liquor, and (3) that compounds like Rochelle salt that hold up the ferric iron in an alkaline solution yield no tannage.† Other gummy bodies such as Irish moss, gum arabic, gum tragacanth,

* Glycerine can be used and seems to yield a tannage giving a soft, red, transparent leather.

† This speaks strongly of the chemical theory of leather formation in iron tannage.

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etc., have hardly any effect. The presence of a chromic salt or an aluminum salt in the iron liquor yielding the corresponding hydroxide in an alkaline solution has some tendency to hold up the precipitation of iron as ferric hydroxide and thus stabilizes it, especially when the amount present is equal to or greater than that of the iron, but this works best in a solution so alkaline as to peptize the chromic hydroxide or aluminium hydroxide.[30] To regulate the speed of precipitation and also of the tanning action of iron in the pelt there is, at present, no satisfactory way except by the careful adjustment of the basicity of the iron liquor and of the control in subsequent neutralization.

To minimize the interference of iron in the leather with dyeing, it is found that if the neutralized tanned pelt is first dried to "crust" before coloring, the iron appears better fixed in the fiber and its chemical activity greatly lessened. The use of pyrogallol tannins such as sumac, oak, etc., or certain less astringent catechol tannins such as mimosa, gambier, etc., then gives only a light grayish color so that these tannins can be used for mordanting as can also other vegetable matter such as fustic, etc., that do not produce a decided black with iron when used in small quantities. To keep the leather soft and flexible it is generally advisable to apply a somewhat heavy fat liquoring, or an oil re-tan using marine oils such as cod liver oil, shark liver oil, etc.

Section 9. Chrome-Iron Joint Tannage.

This form of joint tannage from the use of sodium dichromate as the oxidizing agent for iron proved to be very successful. It did not give a pure iron tannage, but a joint tannage of the chrome as well as iron. The relative amount of tannage due to each in the resulting leather is dependent upon the relative quantity of each present in the liquor.

From the invention of the Augustus Schultz's two-bath chrome process, it has been established that a dichromate, or chromium in the hexavalent state, has little or no tanning property until after it is reduced to the chromic (trivalent) state, Cr^{+++}. It was

[30] Cf. "Hydrous Chromic Oxide" by C. F. Nagel, Jr., *Jour. Phys. Chem.*, Vol. 19, p. 331 (1915).

Also "On the Behavior of Some Oxides with Caustic Potash in the Presence of Oxide of Chromium" by Northcote and Church, Vol. 6, p. 54 (1853).

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seen* that ferrous iron had no tanning property until after it was oxidized to the ferric state. Considering the properties of the two salts it is evident that a combination of the two is a natural outcome, using one as the oxidizing agent and the other as the reducing agent, both being benefited by the reaction mutually engaged in so that a joint tannage results. From the chrome tannage point of view, the use of the ferrous salt as a reducing agent possesses some advantages over the other reducing agents such as sodium bisulphite, sodium thiosulphate, sulphurous acid, glucose, glycerine, etc. For, unlike these latter which generally leave inert substances in the bath after the reduction reaction and which contribute nothing beyond the reduction of the chromate,† the ferric salt formed from the reduction reaction of the ferrous salt can be utilized as a tanning agent in the same bath. From the iron tannage point of view, the choice of the dichromate as an oxidizing agent is prompted by many considerations. First, as an oxidizing agent its oxidation potential is high and the oxidation reaction rapid, proceeding to completion in the cold. Second, for its oxidation action it requires only a very low acidity‡ in the solution so that the basicity of the resulting iron liquor is completely under control. Third, the waste product from the oxidation reaction, namely, the chrome salt, is a valuable tanning agent which can contribute fully to its share in the resulting tannage. Fourth, the green color of the chrome tannage has the effect of neutralizing the red-yellow color of the iron, yielding a product of a less pronounced color. One possible drawback in the use of iron as the reducing agent for the chromate might be that the quantity of the ferrous salt used is comparatively large (5½ parts of $FeSO_4.7H_2O$ to 1 part of $Na_2Cr_2O_7.2H_2O$ by weight) especially when the commercial copperas has been partially air-oxidized, and that the color of the product is somewhat darker (brownish) than when other reducing agents are used with the chromate (light green). But for a certain class of goods this is not objectionable, and advantage can well be taken of the lower

* Section 8, page 229, footnote.

† In case sodium thiosulphate is used as the reducing agent, the colloidal sulphur may contribute some tannage, and it gives a lighter color to the leather.

‡ Contrast the case where a chlorate is used as the oxidizing agent.

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cost of production. It is important that the basicity of the bath be carefully adjusted,* otherwise the bath may be either too acid for the chrome or too alkaline for the iron, so that joint tannage can not be brought about. In general, an amount of 66° Bé. sulphuric acid equal to from 30-35 per cent. of the copperas employed with a sufficient amount of the sodium dichromate for complete oxidation is found to work well.

The following procedure may illustrate the mode of tannage in actual tannery practice. The percentages given are all calculated on the basis of the weight of the drained, pickled pelt (sheepskins, calfskins, etc.). For convenience, the weight of the skins is taken as basis to figure the quantities used. By "gal. %" (gallons per cent.) is meant gallons of the liquid in question per 100 pounds of the skin. For goatskins a somewhat larger quantity should be taken, say 10-20 per cent. greater. The examples given apply to drum tanning.

	Per cent.
(I) Copperas ($FeSO_4.7H_2O$)	11
Salt (NaCl)	5
Sulphuric acid (66° Bé. H_2SO_4)	1½
Water for solution (total)	12 gal.

Drum pelt in the solution for ½ hour, then introduce a solution of

	Per cent.
Sodium dichromate ($Na_2Cr_2O_7.2H_2O$)	2¼
Water to dissolve	2 gal.

Drum for about 1½ hours. (See if all iron is oxidized.) Add very slowly in portions, preferably through the trunnion, a solution of

	Per cent.
Soda ash (Na_2CO_3)	4½
Water to dissolve	3 gal.

After all the alkali is in, drum for 10 minutes longer. (See if the pelt is neutralized.) Rinse. This gives a tannage more of the nature of the iron than the chrome. The following modification can also be employed, if desired.

* Historically Hylten Cavalin came close to the process, but because of lack of proper adjustment for the acidity he failed to obtain a successful tannage (Section 2, page 68).

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	Per cent.
(II) Sodium dichromate ($Na_2Cr_2O_7.2H_2O$)	2¼
Salt (NaCl)	5
Water for solution	12 gal.

Drum the pelt in the solution for ¾ hour. Add to the drum a solution of

	Per cent.
Copperas ($FeSO_4.7H_2O$)	12
Sulphuric acid (66° Bé. H_2SO_4)	2½
Water for solution	4 gal.

Drum for 1½ hours. (See that all chrome is reduced.) Run out excess spent liquor. Then introduce a suspension of

	Per cent.
Bleaching powder	1½
Water	3 gal.

Drum for 15 minutes. Introduce very slowly as before a solution of

	Per cent.
Soda ash	3½
Water to dissolve	3 gal.

After all alkali is in, drum for 10 minutes longer. (See if the pelt is neutral.) Rinse. This gives a tannage more of the nature of chrome than iron.

(III) For one-bath tannage.

(a) When the liquor is to be prepared, take for each 100 pounds of the pelt

	Per cent.
Copperas ($FeSO_4.7H_2O$)	11
Sulphuric acid (66° Bé. H_2SO_4)	3
Salt (NaCl)	5
Sodium dichromate ($Na_2Cr_2O_7.2H_2O$)	2¼
Water (total) for solution	15 gal.

(Add the dichromate very slowly when stirring. Use the liquor without unnecessary delay.)

(b) When a concentrated one-bath is already made according to the method of preparation given in Section 3, take

	Per cent.
Chrome-iron liquor (concentrated)	3 gal.
Water to dilute	12 gal.
Soda ash (Na_2CO_3) to neutralize	½

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In either case, drum the pelt in the liquor for 1 to 1½ hours, or until the pelt is struck through.

Introduce very slowly as before

	Per cent.
Soda ash (Na_2CO_3)	5
Water to dissolve	4 gal.

After all the alkali is in, drum for 10 minutes longer. (See if the pelt is neutral.) Rinse.

The stock tanned by any of the above processes should be soft and full. It has a color varying from a dull yellow, grayish brown, to olive drab, depending upon the proportion of the chrome to the iron present. To secure the predominating effect of the chrome tannage, some chromic salt may be added to the liquor. The leather obtained does not stand boiling unless the chrome content is increased by the addition of a chromic salt to the liquor.

The leather can be dyed black with logwood with or without a "striker." It can be dyed with coal tar dyes, such as the acid, direct, and alizarine dyes. When it is to be dyed with a basic dye a mordant is required, in which case, the tanned stock is best first dried to "crust" and then wetted back for mordanting with fustic or other vegetable matter after which the basic dye is applied in the usual manner. For fat-liquoring a somewhat larger quantity of the fat-liquor (5-8 per cent. of "sulphonated" cod liver oil, degras, "sulphonated" Neat's foot oil, or a commercially prepared mixture) can be used. The proper temperature for dyeing is between 130°-140° F. and that for fat-liquoring 110°-120° F.

The leather can be re-tanned in oil to advantage when cod liver oil or other fish oil may be used. It can be re-tanned and colored black in ordinary vegetable tannins. Some basic black can be used for topping. When a less astringent tannin is used, a light gray color is obtained. In such cases, drying to "crust" prior to the treatment is advisable.

A sample of sheepskin leather tanned according to (I) above gives the following analysis:

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	Per cent.
Moisture	7.43
Ash	15.69
Fat	21.48
Fe_2O_3	10.51
Cr_2O_3	1.84
*P_2O_5	2.50
SO_3 (total)	2.12
Hide substance (N × 5.62)	43.85

* From some disodium phosphate introduced together with the alkali for neutralization.

Section 10. Pure Iron Tannage.

As it is desired to determine the actual tanning value of a ferric salt, a considerable portion of the time has been devoted to the study of the pure iron tannage, that is to say, to the tannage where no other metals except iron that can yield a tannage are present. It has been often reported that iron tannage produces a brittle leather, a leather that draws together on drying, a leather that deteriorates on keeping, and so on. One of the arguments advanced is that iron in the leather acts as an oxygen carrier, taking in oxygen from the air and imparting it to the fiber, so that the fiber is gradually oxidized and corroded in the course of time.[31] It has so far not been found possible to confirm this report, but, on the other hand, there is sufficient evidence to show that any defect of this kind is due to an improper tannage rather than to the inherent nature of the tannage. For, when a leather is properly tanned, it is not at all brittle, does not draw together hard on drying, nor behave in any way different from other mineral tannage. Samples of sheepskin leather tanned with iron salts that have now been kept for more than ten months show no sign of deterioration of the sort reported. It is probable that these defects were brought about by the use of a too alkaline iron liquor in which ferric oxide had been caused to deposit on the surface, making the interior of the pelt impenetrable to the tanning agent. Too rapid a neutralization would also cause the same defect, as the ferric oxide which is caused to separate from the solution would coat the surface of the pelt. This gives rise to a hard outer layer (grain) and a wide soft zone underneath in the cross section of the pelt.

[31] "Die moderne Leder-Fabrikation" by Hermann Zeidler, p. 109 (1914).

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As it is the ferric iron that possesses the tanning property, it follows that all iron should be kept in the ferric state. It is not so much, however, to avoid a small loss of iron going to the ferrous state as to prevent the ferrous iron finding its way to the pelt causing irregularities in appearance and texture in the leather. Hence it is necessary to use a sufficient quantity of a proper oxidizing agent to bring about complete oxidation, and not only that, to use a small excess of the oxidizing agent (10-15 per cent.) to take care of any subsequent reduction. To insure this, a further guaranty is found in the introduction of a small quantity of a suitable oxidizing agent ($Na_2Cr_2O_7.2H_2O$, CaClO.Cl, etc.) toward the end of the tanning process, prior to the neutralization—the so-called after oxidation. This is a proper action at this stage, inasmuch as the oxidation reaction involves a decrease of hydrogen ion concentration in the solution, thus helping to fix the iron in the pelt .

The best basicity for the tan liquor is found to lie in a range varying between the ratio of 5 equivalents of the mineral acid radical (or radicals) present to every 6 equivalents of the ferric iron, and that of 3 equivalents of the mineral acid radical (or radicals) present to every 4 equivalents of the ferric iron. When much iron salt in the liquor is in the form of a sulphate, it is safer not to go too near the higher limit of basicity. For if such is the case a light yellow hydrated ferric oxide (not a red gelatinous ferric hydroxide) would then be thrown out on short standing. It is evident that the same danger of rapid precipitation exists during neutralization. Hence it is necessary to effect the neutralization very gradually. The total amount of an alkali needed for neutralization is only 70-80 per cent. of the theoretical.

For the oxidation of iron and the preparation of the tan liquor from a ferrous salt, chlorine is found to work very satisfactorily, as it can effect the oxidation in the cold in the absence of any acid and push the reaction to completion under a small pressure.* Other suitable methods of oxidation are those using nitric acid and sulphuric acid, and sodium nitrate and sulphuric acid. The latter is more economical because of the cheapness of the sodium nitrate (Chile saltpetre) employed. All methods involving the

* For detailed directions concerning the preparation of the tan liquor, see Section 3.

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use of nitric acid in one form or another, however, require a boiling temperature, and hence a special container to resist the corrosive action of the hot nitric acid.

For tanning, a quantity of ferrous sulphate crystals, $FeSO_4.7H_2O$, between 12 and 15 per cent. of the weight of the drained pelt is generally sufficient, the higher figure being for heavy hides and for the goat skin. A rough guide to secure the correct basicity for tanning is to add 10-14 per cent. of soda ash, Na_2CO_3, of the weight of the ferrous sulphate crystals taken. This presumes that the ferric liquor to start with is neutral in composition.

The following method for sheepskins in drum tanning can be used for illustration. Unless otherwise stated, all percentages are on the basis of the weight of the drained pelt. When the stock to be tanned is much below 100 pounds some judgment should be exercised in regard to the modification of these percentages.

	Per cent.
Iron liquor containing an amount of Fe_2O_3 equal to....	3½
(or as $FeSO_4.7H_2O$	12)
Salt, NaCl	4
Soda ash, Na_2CO_3	1½
Total volume for tanning.....	25 gal.

Drum for 1 to 1½ hours. Introduce into the drum a suspension containing

	Per cent.
Bleaching powder, CaClO.Cl	1¼
Water	1 gal.

Drum for 15 minutes longer. Neutralize the pelt very gradually (in small portions) with a solution of

	Per cent.
Soda ash, Na_2CO_3	4
Water to dissolve	3 gal.

After the alkali is all fed in, drum for 10 minutes longer. Rinse. Hang the tanned pelt to dry. Sammy back from "crust" and wet thoroughly for subsequent operations.

For a coloring black, use

	Per cent.
Hematine crystals	1½
Water to dissolve equal to twice the weight of the wet stock	

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Make the solution alkaline with ammonia, and heat to 130° F. Drum for 30 minutes and then add to the drum a solution warmed to 130° F. containing

	Per cent.
Basic leather black	1
Water to dissolve	5 gal.

Drum for 20 minutes, or until the leather is colored through. Run off the spent dye liquor. Fat-liquor with an emulsion at 130° F. containing

	Per cent.
"Sulphonated" cod liver oil	6
Water	80

Drum for 45 minutes, or until all fat-liquor is taken up. Hang the fat-liquored stock to dry without setting out. Any commercial fat-liquor mixture can be used.

For such a black leather, however, a re-tan in ordinary vegetable tannins is more economical and advantageous, since the vegetable tannin not only gives a black color but also a tannage to the leather. Consequently the leather obtained is fuller. For such purpose, use a tannin liquor, warmed to 110° F., containing, say,

	Per cent.
Quebracho liquid extract	15
Water	120

or a tannin liquor having a barkometer reading of from 15° to 20° Bk. Drum for 1½ to 2 hours. This generally gives a grayish black color. To obtain a deeper black color, top the leather with 1 per cent. basic leather black in the usual manner. This method of blacking dispenses with the logwood color and even with the "iron striker." For a light (silver) gray color, pyrogallol tannins, such as pure oakwood tannin, sumac, etc., or a less astringent catechol tannin, such as mimosa, gambier, etc., can be used. This vegetable re-tan, however, can best be carried out in a paddle.

In the case of heavy leather, an oil re-tan can be applied to advantage, using, say,

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	Per cent.
Dégras	8
"Sulphonated" cod oil	4
Water	12 gal.

Drum for 1½ hours with the mixture warmed to 130° F. (At present shark liver oil is available and can be utilized for this oil re-tan.) Or, the leather may be stuffed with a mixture of stearin, tallow, and "sulphonated" cod oil, using, for example,

	Per cent.
Stearin	4
Tallow	10
"Sulphonated" cod oil	8

Heat the fat mixture to 150° F. in the drum, and drum for about ½ hour.

In general, an iron tanned leather is tough, heavy, but somewhat harsh. Hence it is generally advantageous to give the leather a good far-liquoring, or oil stuffing, or oil re-tan. It does not resist a boiling temperature but begins to contract at about 170° F. or lower.

For dyeing the iron tanned leather with basic dyes, the remarks made in Sections 8 and 9 apply here with a greater force.

A sheepskin leather tanned with 8 per cent. $Fe_2(SO_4)_3$, 4 per cent. NaCl, and 1.6 per cent. Na_2CO_3, subsequently neutralized with 4½ per cent. $CaCO_3$, and finally lightly fat-liquored with a mixture of neat's foot oil and a mineral oil, gives the following analysis:

	Per cent.	
Moisture	14.10	
Fat	5.37	
Ash	20.01	
Fe_2O_3	4.08	
SO_3 (total)	3.26	
Hide substance	51.22	($N \times 5.62$)

This sample of sheepskin leather is tough and full, but feels somewhat harsh. It has a beautiful yellow-red color. From the analysis of the iron content, it seems that an amount of iron as low as 4 per cent. Fe_2O_3 of the weight of the air-dried sample is sufficient to give a satisfactory tannage.

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Calcium carbonate (or the "precipitated lime") or magnesium carbonate is found to be very suitable for neutralization in place of, or together with, soda ash. It is cheap and can be used in excess to prevent the presence of any free mineral acid (H_2SO_4) in the leather. The calcium or magnesium sulphate formed in the leather during neutralization, furthermore, serves to give weight to the leather.

It might also be mentioned that in a tannery where chrome or vegetable tannage is employed, the presence of an iron salt is incompatible with good appearance of leather and all possible care is to be taken to keep away any iron from all liquors. In iron tannage this difficulty disappears.

Section XI.—Iron Phosphate Tannage.

As the iron-tanned leather has a pronounced red-yellow color and as iron is capable of forming many colored bodies both with the organic and inorganic substances, attention is naturally drawn to the utilization of this chemical activity of iron for coloring the leather by a treatment with a substance which combines with iron to give the color. At the same time, it should be equally possible to find a substance that will give with iron a color lighter than that of the iron leather itself. In general, these combinations are in the form of a precipitate. Thus, Knapp treated his iron leather with a fatty acid forming a yellow precipitate of "iron soap" in the leather.[32] He was not, however, so much concerned with the yellowish brown color of the "iron soap" as with the fixation of iron in the leather so that it could not be washed out. The use of potassium ferrocyanide solution for producing a blue color has been mentioned.[33] But it is found that the color is not fast and is gradually washed out, especially when the leather after such a treatment is not immediately fat-liquored; and, if the pelt is treated with the ferrocyanide solution before the iron has been fixed in the leather, a very poor tannage is obtained. Logwood (for dull black color) and fustic (for green-black color) coloring matters have been long known in their use with iron (as a "striker"); but while they give a fast color, they contribute no material tannage. And it is said that much excess of

[32] British Patent No. 2,716 (1861).

[33] "A Text Book of Tanning," by H. R. Procter, p. 222 (1885).

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iron should be avoided as it would render the leather brittle and liable to crack.[34] A soluble sulphide or polysulphide has been advocated for making black leather in connection with the iron tannage by O. Röhm,[35] but there are grave doubts as to its practicability, because these alkaline or alkaline earth sulphides generally have a strong reducing action, and the black ferrous sulphide formed is merely a filler and not a tanning agent for the pelt.

It is found feasible, however, to make the black or grayish leather by re-tanning the iron leather in ordinary vegetable tannins. This not merely gives the color, but also involves a further tanning action. The leather thus obtained partakes of the characteristics of both the mineral and the vegetable tannages.

A scheme of making a light colored, or substantially white leather with the use of a phosphate has been satisfactorily worked out. The function of the phosphate seems to be more than producing a yellowish white compound of ferric phosphate in the leather. Borax having a property of forming a light red compound, ferric borate, could be used, but the quantity needed is usually large. It is, however, suitable for neutralization because of its mild alkaline nature. It may be added that other white or yellowish white compounds of iron are the ferric arsenate, and the iodate. Certain features about these substances, such as the poisonous character, the cost, etc., make their use for leather making clearly impracticable.

The idea of using a phosphate in connection with the iron tannage was suggested by the fact that from the colloid chemistry point of view the phosphate ion, being a trivalent negative ion, should act favorably towards the fixation of iron in the pelt. The mode of procedure is illustrated by the processes given below:

I. The pelt to be tanned is drummed in the ferric iron liquor of the same character and basicity as for pure iron tannage* and treated in the same manner up to the neutralization of the pelt. For neutralization, use

[34] "Leather Dressing," by M. C. Lamb, p. 149 (1907).

[35] British Patent No. 103,827 (1917).

* See Section 10 on Pure Iron Tannage.

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	Per cent.
Sodium pyrophosphate, $Na_4P_2O_7.10H_2O$	4
Soda ash, Na_2CO_3	2¼
Water for solution	20

or

Trisodium phosphate, $Na_3PO_4.12H_2O$	6
Soda ash	1¾
Water, same as above	

Introduce the solution slowly in the usual manner. It is found better to introduce the carbonate together with the phosphate than to add the phosphate alone first. Pyrophosphate is preferred because of its high phosphate content for a given weight. Borax may be used together with the phosphate and the carbonate; in which case the amount of the latter used should be correspondingly decreased. This tannage gives a leather of a light color. Subsequent treatments given in Sections IX and X can be followed.

II. The phosphate may be directly added to the ferric tan liquor giving a fine milky suspension. In this case, the addition of the alkali to bring about the proper basicity for tanning should be omitted. For sheepskins in drum tanning, use

	Per cent.
Ferric salt (calculated as $Fe_2(SO_4)_3$)	9
Sodium pyrophosphate, $Na_4P_2O_7.10H_2O$	4
Total volume	15 gal.

Dissolve the pyrophosphate in a small quantity of water and add it to the ferric salt solution slowly with constant stirring. Having stirred thoroughly, introduce it immediately into the drum and tan the pelt for 3 to 5 hours, or until the pelt is thoroughly penetrated. Neutralize the pelt slowly with

	Per cent.
Soda ash, Na_2CO_3	3½
Water to dissolve	3 gal.

After all the alkali is fed in, rinse and hang to dry. This gives an especially white leather. The process is suitable for light stock, such as glove leather and the like. The penetration is somewhat slow, hence a longer drumming is needed. When dried, the leather is full and soft. It becomes velvety after staking and perching.

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The leather can be finished by any of the usual treatments. In dyeing, with basic coal tar dyes, the ordinary precautions in connection with the use of vegetable mordants should be observed. As the leather does not resist a high temperature, it is important not to use a temperature above 140° F. in dyeing or fat-liquoring.

A sample of sheepskin leather treated in accordance with (II) above, but without neutralization or fat-liquoring, gives a soft and almost white leather. Its chemical analysis gives

	Per cent.
Moisture	11.48
Fat	11.75
Ash	12.23
Fe_2O_3	3.97
P_2O_5	2.32
SO_3 (total)	2.15
Hide substance (N × 5.62)	54.90

Here again it shows that about 4 per cent. of iron as Fe_2O_3 on the basis of the air-dried sample is sufficient to give a tannage for light skins.

Section XII.—Conclusions.

The character of the iron tannage seems to lie between that of the alum and that of the chrome tannage. Iron seems to yield a more permanent tannage (towards water) than alum, but like the alum tannage, iron tanned leather does not resist the boiling temperature of water. If we take the critical temperature as that at which the sample under water begins to shrink or to draw together under the influence of heat, that point generally lies between 160°-175° F. In the case of a re-tanned leather (in fish oils or vegetable tannins) a somewhat higher test may be obtained; but in no case can an iron-tanned leather stand boiling, unless considerable portion of the tannage is due to chrome as in the case of the chrome-iron joint tannage.

It has been often reported that iron-tanned leather produces a brittle grain, and rots on storing. To do justice to the iron tannage it must be declared that an iron-tanned leather, properly tanned, is not brittle on the grain and does not deteriorate on storage. Samples of the leather that have now been kept for more than ten months show no sign of deterioration. Sometimes

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the product obtained is somewhat stiff and "flat," but this should not be ascribed to the inherent properties of the tannage. The strength, the fullness, the elasticity are, in our opinion, a matter of proper tannage and not dependent upon the nature of the tannage.

As a considerable amount of salt (4-5 per cent. of the weight of the pelt) is needed in the liquor and much of it is formed from neutralization, it is important to rinse the tanned stock after neutralization to wash off most of the neutral salts present (NaCl, Na_2SO_4, etc.); otherwise their presence in the leather may cause dampness or even salt stains or spues. Iron tannage is much affected by the presence of grease or any imperfections in the skins, and when such is the case, unevenness of color and other irregularities are liable to show up on drying. Hence the necessity of uniform softening of the pelt and of degreasing.

Iron-tanned leather generally runs high in ash. The leather has oftentimes a harsh feel, due probably to the presence of a large amount of iron oxide (Fe_2O_3) in the leather. Because of the harsh feel it is generally advisable to give the leather a somewhat heavy fat-liquoring or an oil treatment. The use of flour, egg yolk, etc., may be practiced, if desired. At the present stage of our knowledge it seems that to produce a satisfactory tannage at least for a light leather an amount of iron calculated as Fe_2O_3 not less than 4 per cent. of the weight of the air-dried sample should be present.

The iron-tanned leather compares favorably with other mineral tanned leather. The red-yellow or brown-red color of the tannage, however, is for some purposes an undesirable feature. The chemical activity of iron in the leather forming dark colored compounds in the leather is another drawback. But even with all these limitations, there is much to be said in its favor. There are certain classes of goods in which these features are of no consequence and the saving in the cost of production is very material. True, there are difficulties in connection with the tanning operation and subsequent treatment of the leather—difficulties which in other tannages either do not exist, or are less serious. But the process, like any other new process, necessitates a new set of conditions. To summarize, the following main factors may be mentioned:

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I. Completeness in the oxidation of iron and maintenance in its ferric state by using an excess of a proper oxidizing agent, and by means of an after oxidation.

II. Adjustment of proper basicity by the addition of a proper amount of an alkali, a basicity between the ratio of one OH^- equivalent to every 5 equivalents of the mineral acid radical present, and that of one OH^- equivalent to every 3 equivalents of the mineral acid radical present, being the proper range for tanning.

III. Gradual neutralization to be effected so that iron may be uniformly fixed in the pelt throughout its thickness.

IV. Drying to the "crust" state before subsequent treatment to minimize the chemical reactions between the iron in the stock and the substances employed that would react with iron to give an undesirable color.

It should not be omitted to mention that the subject of iron tannage presents a broad unexplored field and that this study is far from being exhaustive. Other phases could have been taken up and it is hoped that this work will serve as an indication for much that remains to be done.

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APPENDIX.—A TENTATIVE PROCEDURE FOR THE ORDINARY CHEMICAL ANALYSIS OF IRON-TANNED LEATHER.

With more new chemicals introduced in the manufacture of leather, the chemical analysis of the leather naturally becomes more complicated. The following is a proposed system of the chemical analysis for iron-tanned leather ordinarily sufficient for commercial work. With the exception of the determination of

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free mineral acid, all procedures here given have been tested and found to give satisfactory results. While there are but few features in these methods, the details of the procedure, and the quantities of the reagents to be taken, etc., are those actually found to work well. The determination of the free mineral acid is based on the Procter and Searle's method, and that of the hide substance is adapted from the Dyer's modification of the Kjeldahl method for nitrogen. In order to bring out certain points in the analysis more clearly, notes have been added to each procedure, based upon the results of observations in the laboratory. The order and the grouping of the determinations as found to be convenient are shown as follows:

(1) Moisture } in one sample
(2) Fat }

(3) Ash }
(4) Fe_2O_3 } in one sample
(5) Cr_2O_3 }

(6) Free mineral acid }
(7) P_2O_5 } in one sample
(8) SO_3 (total) }

(9) Hide substance

When only isolated determinations are desired, this order, of course, need not be followed.

Sampling.—Leather to be analyzed should be reduced to small pieces of approximately uniform size. Heavy leather can be shaved with a planer and ground in a small mill. Light leather should be chipped or shredded to pieces of about ¼ inch long by 1/16 inch wide with the natural thickness of the skin. A composite sample should be made from different parts of the whole piece and the sample intimately mixed before a portion is taken for analysis. The prepared sample should be kept in a tightly stoppered bottle.

1. *Moisture.*—Weigh 8 grams of the air-dried sample into a tared glass dish and dry for 8 hours in an electric oven regulated at 99°-101° C. The loss in weight represents moisture.

$$\left(\text{Per cent. moisture} = 100 \times \frac{\text{loss in wt.}}{\text{wt. sample}}.\right)$$

NOTE 1.—The leather should not be exposed to a higher temperature or heated for an unnecessary length of time because any drying oil (cod liver oil, shark liver oil, etc.) used for

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fat-liquoring, oiling, stuffing, or re-tanning would be oxidized to a greater extent. This not only gives low result for moisture, but also for fat determination, as petroleum ether will not dissolve the oxidized fat.

NOTE 2.—The dried sample should be weighed rapidly as it quickly absorbs moisture from the air.

2. *Fat.*—Transfer the sample from the moisture determination to a Soxhlet extractor using petroleum ether (redistilled if necessary using distillate below 60° C.). Fill the dry, clean Soxhlet flask with 160-180 cubic centimeters petroleum ether (to about three-fourths full). Heat the flask in an electric heater (or over a water bath) for 8 hours after which distill the main portion of the ether from the flask into the thimble chamber, collecting this portion. Transfer the ether solution of the fat to a tared evaporating dish, evaporate off most of the ether over a steam bath, and dry the fat at 99°-101° C. in an electric oven for 2 hours. The content of the dish is fat.

$$\left(\text{Per cent. fat} = 100 \times \frac{\text{wt. of fat}}{\text{wt. sample}}.\right)$$

NOTE 1.—To prepare the thimble for extraction. wash the thimble (S. & S.) in a small portion of the ether. Line the bottom of this thimble with a tuft of absorbent cotton that has also been washed in the ether. Place the sample in the thimble and cover it with another tuft of the washed cotton. This size of the sample, together with the cotton lining and covering will be just comfortably contained in the thimble. The thimble prepared in this way will prevent any fine particles of leather from being sucked out through the bottom during syphoning, or from floating off the top when the thimble is completely covered by the ether. A piece of heavy glass tubing can be placed at the bottom of the chamber underneath the thimble to allow some clearance so that the ether can be completely drained from the thimble during syphoning. A small tuft of cotton may be loosely placed at the opening of the condenser above.

NOTE 2.—The same precaution in drying given in Note 1 under moisture determination applies here. When mineral oil is present in the fat extraction it is sometimes difficult to get a constant weight due probably to the mineral oil being constantly decomposed and volatilized off. The dried fat should also be weighed rapidly.

NOTE 3.—There is only a trace of iron salt that is extracted from the leather by the ether.

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3. *Ash.*—Weigh 2 grams of the air-dried sample in a tared platinum dish, platinum crucible, or porcelain crucible and heat first very gently and then to below dull-red heat. Stir the contents occasionally with a platinum wire and heat gently until it is thoroughly ashed. The residue is weighed as ash.

$$\left(\text{Per cent. ash} = 100 \times \frac{\text{wt. of ash}}{\text{wt. sample}}.\right)$$

NOTE 1.—Chlorides of metals are likely to be partially volatilized and lost at a higher temperature. Sulphates of heavy metals are decomposed with the evolution of SO_3 fumes. If the sample is heated too strongly, especially at the beginning, the leather cakes together so that the inner part is difficult to burn off. Sometimes the content fuses when heat is applied too strongly, so that it is hardly possible to transfer the ash to a crucible for alkaline fusion. In this case it is better to use a platinum crucible for the ash determination. But when a phosphate is present, great care should be taken not to cause the reduction of the phosphorus with the result of ruining the platinum crucible.

NOTE 2.—For iron-tanned leather a 2-gram sample is sufficient, as the ash usually runs high.

NOTE 3.—Owing to an inevitable loss of some chlorides and to an indefinite amount of sulphates decomposed, the significance of the ash determination cannot be of great value. Furthermore, unless the manner of heating and other conditions are the same, good checks in different hands are difficult.

4. *Iron.*—The ash from the last determination is fused in a platinum crucible with a well pulverized and intimately stirred mixture containing 1½ grams anhydrous pure K_2CO_3, 1½ grams anhydrous pure Na_2CO_3, and 1½ grams pure borax glass, until the liquid in the crucible appears homogeneous. Cool, meanwhile heating to boiling 150 cubic centimeters of distilled water in a 350 cubic centimeter casserole. Place the crucible in the hot water, cover the casserole with a watch glass, and boil very carefully. Wash out the contents of the crucible, break up the mass, and allow to settle. Filter by decantation, and wash the precipitate with hot water, collecting the filtrate in a 400 cubic centimeter beaker. Ignite the precipitate and weigh as Fe_2O_3.

$$\left(\text{Per cent. } Fe_2O_3 = 100 \times \frac{\text{wt. } Fe_2O_3}{\text{wt. sample}}.\right)$$

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NOTE 1.—Only a trace of iron is found to pass into the filtrate. If desired, the precipitate on the filter can be dissolved with 20 cubic centimeters hot dilute HCl (1 conc. HCl : 2 water by vol.) and the ferric hydroxide precipitated again with NH_4OH with the addition of 2 grams NH_4Cl. Or, the iron in the HCl solution can be determined by the Zimmermann-Reinhardt volumetric method, taking care to oxidize off all organic matter with $KMnO_4$ before $SnCl_2$ reduction.

5. *Chromium.*—Cool the filtrate from the iron determination and make it up to 250 cubic centimeters. Pipette 100 cubic centimeters of the filtrate into a 500 cubic centimeter beaker. Dilute to about 200 cubic centimeters. Acidify with concentrated HCl and add 5 cubic centimeters in excess. Add 15 cubic centimeters of 15 per cent. KI solution and titrate with N/10 sodium thiosulphate solution, adding 1 cubic centimeter of thin, clear starch solution after the color of the solution has changed from red to light yellow. Titrate to the disappearance of the blue color.

$$(\text{Per cent. } Cr_2O_3 = 100 \times \frac{\text{cc. N/10 } Na_2S_2O_3 \times 0.002533}{\text{wt. sample}} \times 2.5).$$

NOTE 1.—When the chromium present is small, the orange color of the dichromate cannot be distinguished. Hence the acidification should be guided by a litmus paper.

NOTE 2.—A thin, clear starch solution that can keep for several months is prepared as follows: Take 1 gram ordinary starch powder and rub it into a paste with 25 cubic centimeters distilled water. Heat 200 cubic centimeters distilled water to boiling and stir the thin paste into the hot water. Boil for a few minutes when a transparent solution will be obtained. Filter the solution through absorbent cotton into a 250 cubic centimeter glass stoppered bottle. Add 5 cubic centimeters chloroform, stopper the bottle and shake.

NOTE 3.—When chromium in the iron tan liquor is to be determined, pipette 25 cubic centimeters of the sample in a 250 cubic centimeter graduated flask. Make up to the mark. Take 25 cubic centimeters and dilute to 35 cubic centimeters with distilled water. Oxidize the chromium with Na_2O_2 by adding small portions at a time with constant shaking; 1½ to 3 grams Na_2O_2 is sufficient for a sample containing 15 to 30 milligrams Cr_2O_3. After all the Na_2O_2 has been added, heat the solution until the volume remaining is about 10 cubic centimeters. Add 25 cubic centimeters distilled water and evaporate down to this

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same volume again. Dilute to about 150 cubic centimeters, bring to a boil, allow to settle and filter off the Fe_2O_3, collecting the filtrate in a 350 cubic centimeter beaker. Wash the precipitate with hot distilled water, collecting it with the filtrate. Determine chromium in the filtrate as before.[36] Ignite the precipitate and weigh as Fe_2O_3.

(Remark: Excess of Na_2O_2 used must be completely decomposed or a phenomena of the reappearance of the starch blue color shortly after it is discharged will occur, making the determination worthless.)[37]

6. *Free Mineral Acid* (Based on Procter and Searle's Method). —Weigh 2-gram sample in a platinum dish. Cover the sample with 25 cubic centimeters N/10 Na_2CO_3 (accurately titrated against the HCl used below). Allow the sample to wet thoroughly and evaporate to dryness on a water bath. Gently char the organic matter, cover with about 50 cubic centimeters hot distilled water, stir, and break up the mass. Filter into a 250 cubic centimeter beaker. Return the residue with the filter to the dish, and ignite gently. Cool and take up the ash with 25 cubic centimeters N/10 HCl. Filter into the previous filtrate and wash thoroughly. Add 1-2 drops methyl orange, and if red color is seen, titrate with N/10 alkali.

(Per cent. free mineral acid =

$$100 \times \frac{\text{cc. N/10 NaOH} \times 0.0049}{\text{wt. sample}} \text{ as } H_2SO_4.)$$

NOTE 1.—This method has not been tested. A full discussion is found in "Leather Industries Laboratory Book" by H. R. Procter, pp. 367-73 (1919). From the experience with chrome leather analysis, we found that sometimes the color of the filtrate was so dark that it interfered with the methyl orange color in titration.

7. *Phosphate.*—Ignite the residue from the last determination together with the filter paper in a platinum crucible. Fuse with 1 gram pure anhydrous K_2CO_3, 1 gram pure anhydrous Na_2CO_3, and 1 gram pure borax glass until the liquid appears homogeneous. Dissolve out the content of the crucible as described under iron

[36] See Section 4, p. 155, footnote.

[37] See "On the Volumetric Determination of Chromium in Chrome Leather" by Te-Pang Hou, JOUR. Am. Lea. Chem. Assoc., p. 367 (1920).

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determination above, filter and wash, combining the filtrate with the solution from the alkali titration for Free Mineral Acid. Acidify the solution slightly with HCl. Add 2 grams NH_4Cl and 15 cubic centimeters magnesia mixture and heat to boiling. Cool in ice water and add ammonia very slowly at first until the solution smells of ammonia on stirring. Add one-fifth of the volume of the solution of concentrated ammonia and allow to stand at room temperature for about 30 minutes. Filter by decantation and wash with water to which 2-3 per cent. ammonia has been added. Ignite the precipitate in a tared porcelain crucible first gently and then strongly with a blast burner or a large burner. Weigh as $Mg_2P_2O_7$.

$$\left(\text{Per cent. } P_2O_5 = 100 \times \frac{\text{wt. } Mg_2P_2O_7 \times 0.6376}{\text{wt. sample}}.\right)$$

NOTE 1.—It has been found that precipitating $MgNH_4PO_4$ in a hot solution gives a purer precipitate of this composition. See that a crystalline but not a milky precipitate results on the addition of ammonia.[35]

8. *Total Sulphate.*—Acidify the filtrate from the phosphate determination with concentrated HCl and add 5 cubic centimeters in excess. Boil to expel CO_2. Add 15 cubic centimeters N $BaCl_2$ solution very slowly with constant stirring. Allow to stand in a warm place for from 2 to 4 hours. Filter by decantation and wash thoroughly with hot water. Ignite and weigh as $BaSO_4$.

$$\left(\text{Per cent. } SO_3 = 100 \times \frac{\text{wt. } BaSO_4 \times 0.3429}{\text{wt. sample}}.\right)$$

NOTE 1.—The total sulphate determination by the alkaline treatment and fusion includes the free sulphuric acid (if any), the neutral sulphates, and the sulphate from the oxidation of sulphur in the protein substance (if no SO_3 is lost). With sufficient alkali present and with slow heating, no material amount of SO_3 should be volatilized during heating.

NOTE 2.—If the total sulphate alone is to be determined the following method proves to be convenient and satisfactory.

Weigh a 2-gram air-dried sample in a platinum crucible, cover it with 15 cubic centimeters of N/5 Na_2CO_3 (approximately) and allow the sample to be thoroughly soaked in the alkali. Evaporate to dryness in an air bath (made by

[35] Compare "Analytical Chemistry," Vol. II, by F. P. Treadwell, translated by Hall, p. 434 (1919).

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setting the crucible into a hole cut in a piece of asbestos board so that about one-fifth of the height of the crucible projects above the board, and placing the board with the crucible on an iron crucible of about 50 cubic centimeters capacity). When the sample is thoroughly dried, gently char it over a very low flame. Fuse the charred sample with 2½ grams K_2CO_3, 2½ grams Na_2CO_3, and 2½ grams borax (all chemically pure) after mixing them thoroughly. Dissolve out the mass as described above. (Fe_2O_3 can be determined here in the precipitate.) Acidify the filtrate with concentrated HCl, boil to expel CO_2 and determine SO_4= by $BaCl_2$ in the usual manner.

Remark: Other methods commonly recommended for the total sulphate determination are based on the destruction of the organic matter by oxidation with (1) fuming nitric acid (Stiasny's method), (2) chromic acid (a dichromate and concentrated H_2SO_4) and (3) sodium peroxide. With fuming nitric acid and chromic it is very difficult to bring the sample into solution even by a prolonged digestion. With the Na_2O_2 fusion, the method is more rapid, but it is accompanied with certain disadvantages. First, that an iron or a nickel crucible, in place of the platinum crucible, must be used and this interferes with the iron determination if it is to be made here; and second, that the frothing and spattering of the liquid during fusion is inevitable (unless the sample is first charred, in which case some SO_2 would be lost). The above method, as described, permits the use of the platinum crucible; gives a very quiet fusion yielding a low-fusing and non-viscous melt; and loses very little, if any, sulphur through volatilization during charring if sufficient alkali (Na_2CO_3) is present in the crucible. On the other hand, too much alkali will cause disintegration of the sample yielding a thick, frothing liquid which takes a long time to dry. The method is somewhat longer than the peroxide fusion.

9. *Hide Substance* (Adapted from Dyer-Kjeldahl Method for the Nitrogen Determination).—Weigh a 1-gram sample, wrap it in a small quantitative filter paper, and introduce it into a dry Kjeldahl flask (250 cubic centimeters capacity). Cover the sample with 25 cubic centimeters chemically pure 1.84 sulphuric acid and place about 0.7 gram mercury or 0.9 gram solid $HgSO_4$ in the flask. Clamp the flask at an inclination of about 60° and heat very gently until no frothing is seen and the black liquid boils quickly. Cool and introduce 15 grams anhydrous Na_2SO_4 and

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three glass beads. Heat until the sample is completely dissolved and the color becomes light yellow. Cool completely and add very carefully about 150 cubic centimeters freshly distilled water, and shake until all is dissolved. Cool in running water. Transfer the solution to a 250 cubic centimeter graduated flask and make up to the mark. Pipette out 100 cubic centimeters into a 750 cubic centimeter R. B. flask, add ½ gram sodium sulphide crystals, $Na_2S.9H_2O$, dissolved in a little water, and allow to settle. Place in the flask three glass beads and three pieces of pumice stone. Make up the volume to about 300 cubic centimeters with freshly distilled water. Dissolve 10 grams NaOH in about 35 cubic centimeters water to which is added a small amount of rosolic acid. Pour the concentrated NaOH solution into the flask quietly down the side without disturbing. Connect the flask with a Hopkins distilling head to a Liebig condenser and distill with the delivery tubing dipped into the bottom of a 500 cubic centimeter Erlenmeyer flask containing 50 cubic centimeters N/10 HCl (accurately standardized), 50 cubic centimeters water and 1-2 drops methyl orange. Distill for about 45 minutes, when about 150 cubic centimeters of the water will have passed over. Titrate the excess of HCl with N/10 NaOH.

(Per cent. hide substance =

$$100 \times \frac{\text{cc. HCl used up} \times 0.00786}{\text{wt. sample}} \times 2.5).$$

NOTE 1.—Introducing the sample into the Kjeldahl flask by wrapping it first with a small quantitative filter paper prevents any fine particles of the sample from sticking to the upper part of the neck.

NOTE 2.—It is necessary not to introduce Na_2SO_4 into the flask until the frothing has completely subsided, otherwise, troublesome foaming on subsequent heating will result. With the above proportion of H_2SO_4 and Na_2SO_4 and with the catalytic effect of mercury, the sample will be brought into a complete solution in 20-30 minutes.

NOTE 3.—Mercury is first precipitated as grayish HgS in an acid solution, because it will react with NH_3 yielding the mercuric ammonia chloride precipitate $Hg.NH_2Cl$ from which NH_3 cannot be readily liberated. The precipitate of HgS does not interfere with the distillation, and quiet boiling prevails throughout. With NaOH introduced in the manner described, the heavier NaOH solution will remain

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at the bottom layer and there is no danger of loss of any ammonia before distillation. The presence of an excess of NaOH is indicated by the purple color of the rosalic acid.

NOTE 4.—The presence of much chloride in the sample will cause some loss of NH_3 during H_2SO_4—Na_2SO_4 digestion, as NH_4Cl is liable to volatilize off with strong heating.

LEATHER NOMENCLATURE.*

By J. H. Yocum and T. A. Faust.

Received March 29, 1921.

The words, terms and language used in defining the various leathers are not always understood by the average leather chemist, especially the younger chemists, and those whose work is not directly in the tanneries, but who nevertheless are very much interested in this industry. The writers thought that a terminology of leathers would be interesting and instructive to most chemists, especially in view of the fact that there is some confusion as to the meaning of certain terms as regards cuts, finishes or essential characteristics determining the particular nomenclature used.

In compiling this data, great assistance was rendered by many friends among the tanners in defining the various terms, and appreciation of same is acknowledged to all those who gave such assistance; special thanks being due to Messrs. Jarvis, Stevenson, Fenlin and King.

SOLE LEATHER.

Acid—Includes nearly all sweat hides and also some limed hides. Before tannage, hides are beamed and colored in clean liquor and then plumped in sulphur acid, resultant leather being very hard and solid.

Bloomed—Heavy yellowish deposit on grain, formed by use of oak bark or valonia for dusting. Not scoured.

Hemlock—Tanned with hemlock bark or admixtures of other material with hemlock giving the hemlock color and characteristics.

Non-Acid—Practically all limed hides used, very few sweats. Hides are put directly into weak liquors which are progressively much stronger, resultant leather being more mellow and flexible.

* NOTE.—Mr. Yocum was engaged with Mr. Faust in the preparation of this article at the time he was taken with the illness which resulted in his death. This, therefore, will be the last of numerous papers contributed to the JOURNAL by him.—EDITOR.

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Oak—Tanned with oak bark or admixtures of other material with oak giving the oak color and characteristics.

Red Leather—Hemlock bark tannage.

Scoured—Before drying, leather is scrubbed to remove all surface accumulations from tan liquors, generally oak.

Union—Originally oak and hemlock; now tanned with mixtures usually of quebracho and chestnut giving a color similar to oak.

CUTS OF SOLE LEATHER.

Back—A side which has the belly and head cut off.

Belly—The flanks and the lower part of the side which is not of good average weight and solidity.

Bend—A back which has the shoulder cut off.

Blocks, Jumbos—Sole leather cut into small pieces usually 8 by 12½ inches.

Crop—A side which has the belly cut off.

Head—Cut off at the flare into the shoulder.

Shoulder—That part between the neck and a line cut across the hide from the center of the front flanks, about 50 inches from the butt of the tail.

Side—The hide is divided into two parts (sides) by cutting down the back bone.

Strips—Bends or backs cut at right angle to back bone, into pieces usually 9 inches wide.

Taps—The front half of a sole sometimes called a half sole.

Top Lifts—Lower part of a heel.

AUTOMOBILE, CARRIAGE AND UPHOLSTERY.

No. 1 Split Up.

Buffing—A very light cut, about one ounce weight taken off the top of the hide, which is used when dyed, for bookbinding, pocketbook work, covering spectacle cases, cameras, etc. This light cut does not take all the grain off the hide, but probably goes a little more than half through the grain.

Machine Buff—This is the next cut after the Buffing and has grain pretty well all over the hide, depending upon how well the Buffing is taken off. It is used for upholstering automobiles, furniture and carriages, after being finished in linseed or dope.

Main Split—This is the next cut after the Machine Buff and is finished in linseed or dope and used for all kinds of upholstering and trimming.

Extra Split—This is the next cut and sometimes has the shoulders on if heavy enough and sometimes not, in which case it is called a "Buff Split" and is used for a variety of purposes. It is sometimes filled with grease and used for cheap shoes and other times finished in dope and used in bag work.

Slab—This is a small leveller off the bottom of the hide and is considerably smaller than the Butt Split, and is finished up for tongues of shoes and other cheap work.

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No. 2 Split Up.

Top Grain—This has the full grain off the top of the hide and measures a little less in substance than the Buffing and Machine Buff combined as in the No. 1 Split Up. It goes right down to the split and does not leave any grain on the hide. It is very often dyed and finished up in various shades with a Spanish effect or in straight colors, and generally used on furniture.

Special Deep Buff—This comes next and is finished in dope or linseed for furniture or other trimming work.

Extra Split—The same as in No. 1 Split Up.

Slab—The same as in No. 1 Split Up.

No. 3 Split Up.

Heavy Buffing—About 2 to 2½ ounces weight which is used for special work such as bookbinding or bag and case.

Special Machine Buff—This is the next cut and has very little grain on it and is rather soft and pliable on account of being so near the top of the hide. It is used for all grades of upholstering.

Main Split—The same as in No. 1 Split Up.

BELTING LEATHER.

Belting Butt—A hide with the head and bellies trimmed off. This is not split down the backbone.

Butt Bend—As above, but in addition the shoulder is cut off, usually 50 inches from butt of tail.

Centre—A strip cut the length of the bend from 12 to 48 inches wide, the backbone being in the middle.

Shoulder—Cut same as sole leather.

Side Strips—The part between the center cut and belly.

HARNESS AND SADDLERY LEATHER.

Backs—Cut same as sole leather.

Bellies—Cut same as sole leather.

Bulls—Bull hides tanned, sold in sides, always thin in shoulders and thick in neck.

Collar Leather—Side leather from very light hides finished in black or russet.

Sides—Cut same as sole leather.

Skirting—Light hides tanned in russet color for light straps, saddle parts, etc.

Stags—Somewhat similar to bulls, but more uniform thickness.

Russet Rein—High grade medium weight leather, carefully levelled and finished light oak color.

LIGHT LEATHERS.

Goat.

Castor—High grade kid leather, principally used for kid gloves.

French Kid—Alum tanned goatskins, rarely made now; very fine leather, but not water resistant.

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Mocha—High grade Arabian goatskins tanned usual way with two-bath chrome.
Morocco—Original name for kid leather.

CALF.

Dongola—Gambier and alum tanned calf.
Kips—Extra heavy calf, small hides.
Veals—Small calf, thin, and fine texture.

SHEEP.

Basils—Unsplit sheepskins, usually quebracho or bark tanned.
Cabretta—The skin is taken from an animal which is a cross between a sheep and a goat. Cabretta leather shows partly the characteristics of both leathers.
Chamois—Oil tanned sheep splits.
French Morocco—Sheepskins, either roans or skivers, usually sumac tanned, and finished similar to kid.
Roans—Sheepskin, not split, usually sumac tanned.
Skiver (Grain)—Grain split of sheepskins, usually bark tanned for hat sweats, bookbinders, pocketbook, etc., leathers.
Split (Flesher)—Flesh split of sheepskin.

MISCELLANEOUS.

Apron Leather—Whole hides are tanned, levelled carefully and grain finished smooth. Used in wool carding machines.
Bag and Case Leather—Light clear grained cow hides, bark tanned, carefully levelled, bleached and finished flat or embossed.
Buckskin (Genuine)—Deer skins tanned with alum and salt, used principally for moccasins.
Buckskin (Artificial)—Chrome tanned calf, grain buffed off.
Calf-Kid—Calfskins tanned in alum-flour-oil mixtures. Finished white.
Colt—Russian horse fronts mostly chrome, used for shoe upper.
Glove Leather—Bark or chrome tanned sheepskins, finished on either flesh or grain.
Indian Tan—Oil tanned light hides.
Innersoling—Heavy splits well retanned.
Jacket Leather—Usually chrome tanned sheepskins, with waterproof finish. Used for leather clothing such as aviators' coats.
Jerken—Suede finished veals.
Kangaroo (Genuine)—Chrome tanned kangaroo skins, finished with glaze on grain, characteristics like Cabretta but much firmer.
Kangaroo (Artificial)—Made from kips and light sides to imitate genuine Kangaroo.
Lace Leather—Hides tanned with alum and salt, and usually stuffed heavy with greases. Very tough, used in lacing belts.
Larrigan—Oil tanned light hides, used largely for moccasins.
Latigo—Alum tanned, finished with gambier, etc., used for halters.

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Napa Leather—Low grade sheepskins tanned with oils and soaps. Usually finished on flesh in white, sometimes finished on grain in black.

Picker Leather—Very soft mellow and tough leather, tanned from steer hides, gambier or oak, sometimes a little alum used. Heavily stuffed, used in textile mills.

Raw Hide—Usually an alum-oil tannage; somewhat similar to lace leather.

Roller Leather—Light good grained sheepskins bark tanned. Used in cotton mills.

Shell Cordovan—Horse Butts—Bark tanned for shoes; also razor strop leather.

Side Cordovan—Horse Fronts—Front part of horse hide tanned with bark, used for shoes.

Skiffings—Levelling from a split, rough tanned, used in harness trade for filling collars, etc.

Wallaby—Skin of animal of the kangaroo family. Tanned similar to kangaroo.

Welting—Medium weight hides, mellow bark tannage, lightly oiled, but no finish put on.

Whip Leather—Heavy calf alum tanned; sometimes gambier used.

FINISHES.

Grain Finishes.

Box Calf—Boarded in four directions shape of square, so as to give heavy grain.

Buff Leather—Black dull side upper leather, lightly buffed.

Enameled—Finished as patent, but the leather is boarded and therefore more flexible; used for automobile and upholstery leather.

Glazed Kid—Goatskins finished with high face by Jack.

Glove Grain—Black dull side upper leather, lightly buffed.

Grain Kid—Boarded.

Gun Metal—Smooth dull black finish.

Hat Sweats—Sheep grains bark tanned and finished with wax.

Levant Grain—Usually bark tanned, carefully split, buffed, lightly embossed and grain well boarded.

Mat Calf or Kid—Smooth dull finish.

Mat Velours—Soft pliable chrome leather, very light weight, emeried and ironed.

Patent—Varnish coat, either linseed or "dope" (pyroxyline); several layers applied and dried by heat, process called Japanning. Used on bark tanned leather for shoe trade.

Pebbled—Embossed with pebble design by running through print rollers.

Russia Leather—Gambier tanned calf, very fine grain.

Satin—Side leather, grain snuffed and bright smooth finish put on.

Snuffed Side—Very light grain removed by emery wheel.

Spanish Leather—Upholstery leather; whole hide grains or buffs bark tanned and finished dark yellow with irregular black figurations.

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Storm Grain—Chrome tanned side leather, finished with heavy coating of oil.
Tipping—Poor grained hides, mellow bark tannage (rarely chrome), lightly oiled and japanned.
Velour—Glazed smooth finished calf.
Walrus Grain—Grain drawn in tanning and heavily embossed in finishing.
Willow—Chrome tanned calf, grain boarded.

SPLIT AND FLESH FINISHES.

Elk—Light hides and heavy kips chrome and alum tanned, finished on flesh.
Glove Split—Heavy bark split, soft finish.
Gusset—Light weight splits for tongue stock.
Ooze—Run on emery wheel to give nappy surface.
Suede—Surfaces made nappy by putting on emery wheel; similar to Ooze.
Wax—Bark tanned and heavily stuffed with greases and finished with coat of tallow to give pliable waterproof leather.

THE DETERMINATION IN LEATHER OF MATTER EXTRACTABLE BY WATER.—

Committee Report.

By John Arthur Wilson, Chairman.

Although various official specifications set definite limits upon the acceptable water-soluble content of leathers, the term, as used, is very indefinite. Many substances, especially those of acid nature, are partly free and partly combined with the collagen, or hide substance, at the moment of sampling. But when the leather is washed to remove the free portion, some of the combined portion is immediately liberated. Moreover, the ratio of combined to uncombined constituents in the leather at the time of sampling varies with the humidity, temperature, and other variable conditions to which leather is normally subjected. Since the collagen compounds are not soluble, it would be illogical to include any of the combined matters as water-soluble, and yet it is impossible by any known method to differentiate between the free and combined portions of the matter which can ultimately be extracted by water. Washing not only removes the soluble matter which was present at the time of sampling, but also decomposes some of the collagen compounds, yielding more soluble matter.

Our present official method does not really give a true indication of the water-soluble content of leather, but only of the matter extractable by water under certain conditions. A determination

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of this sort can have a practical value, if the conditions are sufficiently well defined. For example, a high value obtained for a certain class of leather just before fat-liquoring would indicate that the oil will not be properly distributed throughout the leather unless the leather is washed before fat-liquoring. On the other hand the determination would not be of use in calculating the amount of combined tannin in the leather unless the extraction were complete and the hide-tannin compound not decomposed. A method giving results of value for one purpose might be quite useless for other purposes. It would seem that a general method must include all matter extractable by water and the Committee has sought to devise such a method.

If, as has been claimed,[1] prolonged washing does not decompose the hide-tannin compound to any very appreciable extent, the loss in weight of leather by practically complete extraction with water should be a figure of considerable value. The Committee therefore attempted to determine whether practically complete extraction is possible or the hide-tannin compound would slowly decompose, giving no definite end-point.

Theoretical.

The combination of hide substance, or collagen, with the hydrogen ion of acids may be represented quantitatively by the equation:

$$[R] \times [H^+] = K[RH^+] \qquad (1)$$

where [R] represents the concentration of neutral collagen and K is a constant having the same value for all acids. The collagen ion RH^+ is then capable of combining further with the anion of the acid, or with any negatively charged material, such as tannin, to form the electrically neutral compound RHN:

$$[RH^+] \times [N'] = K_1[RHN] \qquad (2)$$

where K_1 is a constant whose value depends upon the nature of the anion or negatively charged group. The two equations show that the greater the degree of ionization of RHN into RH^+ and N', the greater will be the further decomposition into neutral collagen and hydrogen ion, and hence the more easily will the combined acid or other material be removed from the leather by washing.

[1] Wilson and Kern, *J. Ind. and Eng. Chem.*, XII, 1149 (1920).

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If we shake a liter of quebracho solution containing 5 grams of tannin with 60 grams of dry hide powder, the tannin will be removed from solution to such an extent that the solution will no longer give a positive test with the gelatin-salt reagent. On the other hand, if we shake a liter of solution containing 5 grams of gallic acid with this same amount of hide powder, about half of the acid will remain in solution. Upon washing the powders treated in this way, the one containing tannin will not give up tannin at a sufficient rate to be detected by the gelatin-salt reagent whereas the other will yield up its acid at a very appreciable rate. This shows that collagen gallate is much more highly ionized than collagen tannate.

Most vegetable tanned leathers contain considerable amounts of uncombined tannin which can be removed by washing. This does not mean that all of the collagen is completely converted into collagen tannate. It may be true for the surface collagen, but the diffusion of tannin into the substance of the fibers is extremely slow, especially when the leather is not thoroughly wet. The uncombined tannin is probably most concentrated where the collagen is nearly or quite saturated and absent where the collagen is least saturated. The non-tannin acids are much more readily diffusible than tannin and as they are displaced by tannin will tend to diffuse into the lesser tanned regions in the interior, and enter into combination with unsaturated collagen. The uncombined tannin, being largely in the surface regions, ought therefore to be washed out much more quickly than the non-tannin acids, and this is evidently the case.

The time required for complete extraction of leather by water will depend both upon the rate of diffusion of the extractable matter and upon the rate of decomposition of the collagen compounds. Rise of temperature increases the rate of diffusion, but may either raise or lower the rate of decomposition of the collagen-acid compounds. As a general rule the degree of ionization of organic acids increases up to about 50° C. and then decreases with further rise of temperature. Mechanical agitation, also, would be expected to increase the rate of diffusion.

COMMITTEE MEMBERS.

The experimental part of the work was carried out by the following members:

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Paul Hayes, of Graton & Knight Mfg. Co., Worcester, Mass.
Erwin J. Kern, of A. F. Gallun & Sons Co., Milwaukee, Wis.
R. E. Porter, of Ashland Leather Co., Ashland, Ky.
G. W. Schultz, of Elk Tanning Co., Ridgway, Pa.

EXPERIMENTAL.

In the preliminary part of the work an effort was made to determine the effect of mechanical agitation as well as of change of temperature upon the rate of extraction. The temperatures selected were 30°, 50°, and 95° C. While it was appreciated that a temperature of 95° has a destructive action upon vegetable leathers, it was desired to ascertain what effect this would have upon the amount of matter that could be extracted.

The Chairman's instructions to the Committee were briefly as follows: Weigh off at one time one 2-gram portion of the leather sample for a moisture determination and four 8-gram portions, each to be extracted with petroleum ether in a Soxhlet for 8 hours and then to be left exposed to air over night to free from all solvent. Weigh the dried residue from the petrol extract as fat. Use one portion of the leather for the determination of water-soluble by your regular method. Put each of the remaining samples into a bottle such as is used in tannin analysis. Into one bottle put 100 cubic centimeters water at about 30°, into the next 100 cubic centimeters water at 50°, and into the third bottle 100 cubic centimeters water at 95°. Put all three bottles into shake machine and run for 1 hour. Then filter each solution through a linen cloth into a liter flask, keeping a separate cloth and funnel for each flask. Put the leathers back into their respective bottles and add 100 cubic centimeters each of water at the same temperatures as before. Again shake 1 hour and filter into the same flasks, repeating until each flask contains over 900 cubic centimeters of extract. Cool, make up to a liter, filter through a kaolin paper, and weigh the dried residue of an aliquot portion of the filtrate. Now continue to extract the leather in the same manner until 10 liters of extract have been obtained, or until you are convinced that the leather has been freed from all soluble

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matter. Each leather sample should be kept in 100 cubic centimeters water at room temperature during the over-night periods.

The results of this preliminary work are given in Tables I, II, and III. Leather samples No. 1, No. 2 and No. 4 are sawed samples of sole leather, while No. 3 is a similarly prepared sample of belting leather. A very striking result is that less matter was extracted the higher the temperature, which is contrary to the findings of previous committees. Kern's figures for No. 1 are the only ones showing a greater extraction at 50° than at 30°. All figures obtained at 95° are lower than at either 30° or 50°, but the heat had reduced the leather to a crumbly mass. Tables IV, V, and VI give further data obtained by Schultz and Hayes upon the effect of varying the proportion of water used and time of shaking. Here, however, Schultz obtained greater extractions at 50° than at 30°. In the later work he managed to keep the samples at the higher temperature from falling below 40°, whereas in the general Committee work the temperature was not maintained.

The results obtained did not settle to the satisfaction of the Committee as a whole the question as to whether or not a definite end-point in the extraction can be reached. Since the mechanical agitation proved to be time-consuming and to offer no great advantages over straight percolation, the latter method was adopted for the remainder of the work.

The final instructions follow: Weigh off four 8-gram portions for extraction with petrol and a 2-gram portion for a moisture determination. The fat-free portions, after freeing from solvent, are to be used for the tests. For this purpose use an extractor similar to that described by Reed and Churchill,[2] but either put the samples in alundum thimbles or protect them in some other way so that only soluble matter will be extracted. (A heavy cotton plug in the bottom of the extraction tube serves this purpose.) This precaution is necessary so that the final results may be checked by getting the dry weight of the leather after the extraction. Two samples should be extracted at 30°, or at room temperature, and the other two at 50°. Each extraction should consist of 2 liters from which an aliquot should be dried and weighed Continue to extract the leathers until the residues are too small

[2] This JOURNAL, XIV, 133 (1919).

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to be weighed accurately. Then remove one of the samples at 30° and one of those at 50°, dry slowly in the air, and then to constant weight in the oven. The figures obtained ought to check the sum of the weights of the extracted matter. Continue to extract the remaining two samples with water until twice as much has been used as for the first two. Then dry and weigh the samples for comparison with those extracted with only half as much water.

The results obtained, while very interesting in many respects, are not consistent. Schultz and Hayes apparently continue to extract appreciable quantities of matter even after the 30th liter, whereas Kern obtains an end-point with 26 liters and apparently gets no more than traces extracted by an additional 26 liters, and he worked on the same samples used by Schultz and Hayes. It may be significant that Schultz's average result for 60 liters at 25° is slightly lower than Kern's result for only 26 liters at the same temperature. Porter gets an apparent end-point at room temperature, but his results do not check Kern's at all. This discrepancy could not have been due to sampling, because Kern returned a sample to Porter and each repeated the work, checking himself. Both Porter and Schultz got higher results at 50° than at 30°.

Because of the discrepancies in the experimental results it is hardly possible to draw any very sound conclusions. The Chairman personally is of the opinion that a very definite end-point can be obtained by extracting with water at room temperature and that it is practicable to make complete extractions and to determine the amount of matter extractable by water simply by measuring the loss in weight of the dry leather. This figure will, of course, not remain constant, at least for a considerable period after the date of tanning, but will tend to decrease due to the process known as "aging."

Discussion.

All of the above and copies of the eleven tables were sent to each member, who was asked to put in writing any comments or criticism he might desire to make. The following were received:

G. W. Schultz: The apparent deduction to be made from the work of the Committee according to the preliminary direc-

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tions—that less matter is extracted the higher the temperature is misleading and untrue. The temperatures noted for these extractions, with the exception of those coinciding with room temperatures are only significant from the fact that they are the temperatures of the water when added to the leather samples as immediately after this they are lowered, and after rotating 100 cubic centimeters in a glass bottle for 1 hour they have decreased so as to closely approximate the temperature of the room. In fact the opposite—that more matter is extracted the higher the temperature of the water, at least up to a certain point, as reported by previous investigators—is adequately shown by comparing the results in Table IV with those in Table V. The temperature of the water used in Table IV was 25° C. while in the work for Table V it was attempted to keep the temperature up during the entire time of contact with the leather. This was accomplished by interrupting the shaking and immersing in a water bath at 52° C. periodically. It was impossible to maintain a constant temperature, but it did not go below 40° C. or above 50° C. at any time while in contact with the leather. Hayes' work with the Teas extractor (Table VI) also demonstrates this point.

One reason for the lack of uniformity in the work according to the final instructions is without doubt due to the smallness of the sample used. It is well known that in a sample prepared by sawing there are a number of un-disintegrated pieces of leather of considerable size that are torn off by the saws and that this condition becomes worse the duller the saws. Now these small pieces of leather may contain more or less soluble matter than the average sample or the matter may be less easily extracted from them. It is readily seen that several such pieces included in or excluded from an 8-gram sample may cause a considerable difference while with a 30-gram sample the difference would not be so pronounced.

In my work on this section (Tables VII and VIII) six samples were used for each temperature and all six were run at the same time under identical conditions, using a Reed-Churchill extractor, and it will be seen that there is a wide variation in the results between the several determinations throughout the entire experiment.

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I also think that perhaps the greatest part of the difference between the results obtained by Porter and Kern on sample No. 4 (Tables X and XI) is due to the higher temperature used by Porter in his extraction.

My results lead to the conclusion that the amount of tanning material removed from leather by water is not so much dependent upon the volume of water used as it is upon the temperature and time of contact and that the effect produced by these factors is greatest at the beginning of the extraction. It also appears that the amount of matter extracted by water from a given sample very slowly approaches a maximum which is different for each temperature of extraction, and that extraction can be carried out indefinitely and traces still be obtained.

It is difficult to conceive of properly tanned heavy leathers not being completely saturated with tannin whether they be finished by the long time lay-away process in fairly strong liquors or by drumming and dipping in hot concentrated solutions. If, therefore, we accept our chairman's views of leather formation then there should be no question of removing "combined non-tannins" of the nature of gallic acid since the gallic acid in the collagen-gallic acid combination will have been displaced by the tannin in the presence of an excess of the latter and such acid substances will exist free as water soluble matter. Such being the case the extraction of water soluble matter would be comparatively simple providing the collagen-tannin compound were not hydrolyzed. But it is well known that the question is by no means so simple and there is nothing left to us but to believe that the complexity is due to the removal of what should be called combined tannin. It can be seen from my results, according to the final instructions, that the amount of material removed from the leather by the first 2 liters of solution at 50° C. will average about 25 per cent. more than that at 25° C. and it will also be seen that at the end of the extractions with 60 liters of water this percentage remains approximately the same. This indicates that conditions are such at the beginning of the extraction with water at 50° C. that at least 25 per cent. more material is removed in the first 2 liters than should be called water soluble or uncombined material and therefore I contend that the present official method for the determination of water soluble is already too drastic. It removes

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tannin from the leather, which tannin if it is not irreversibly combined with the hide is at least fixed in the leather to such an extent as to improve the quality of the leather and increase its value. As an example of the removal of tannin from leather by extraction with water at 50° C. the following is given: Water soluble determination was made on a sample taken from a heavily tanned side of leather. In the tanning of this leather the tanning solutions used did not exceed 50 purity at any time and no sugar, salts or oil was added, so that the leather contained nothing but the original constituents of the hide and liquors. The water soluble determinations gave 25.85 per cent. which was composed of 10.50 per cent. non-tannin and 15.35 per cent. tannin. Hence the purity of this extract was about 60. If we take 50 (which was high) as the purity of the final tanning material used, then the purity of the water soluble should not have exceeded this and therefore we can assume that at least 4.85 per cent. of tannin has been removed which cannot strictly be classed as uncombined tannin. This represents 23 per cent. of the material that would have been extracted to give a purity of 50, which percentage is curiously close to the difference between the results found by extraction with water at 50 and 25° C.

R. E. PORTER: I believe it would have been well to have prescribed in the instructions for the Committee work the use of alundum thimbles in the extraction of the leather. This probably would have brought about closer concordance in the results obtained by Kern and myself. However, a fairly thick cotton pad, if previously prepared by boiling in a tannin solution and well cleaned, should not only filter well but should neither give up nor absorb any water soluble matter.

Concerning the question of the effect of high temperatures on the amount of matter extracted from leather, it is interesting to note in Table I that whereas I got higher results than Kern in the 30° and 50° extractions, I got lower at 95°. I do not know what procedure Kern used, but it is possible that the procedure I used involved a little higher temperature than that used by Kern. My procedure consisted in pouring boiling water into a 100 cubic centimeter cylinder and in turn pouring this as quickly as possible into the shaking bottle. The highest temperature ob-

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served in the shaking bottle was 77° C., but it is reasonable to suppose that the leather was momentarily in contact with water at about 90°. If my supposition concerning the two procedures is correct it would further emphasize the point that such high temperature extractions yield less extractive matter than lower temperature extractions. It also seems that this Committee work has brought out the uncertainty as to whether extraction at 50° will yield higher or lower results than for example extraction at 30° C. This would indicate that 50° C. is near the turning point and may be an additional reason to that advanced by Schultz, as well as the chairman's opinion, why 50° is too high a temperature to be prescribed in the official method.

PAUL HAYES: My work would tend to indicate that with prolonged washing of leather, a point may be reached at which the weight of extracted matter becomes quite small and fairly constant. Even after washing with 68 liters of water, however, I was still able to obtain a colored residue. I think that a reasonably definite end-point may be reached in washing leather, but I am not prepared at this time to state what it should be or how it should be stated.

CHAIRMAN'S REPLIES: It would seem well to let speculation regarding the influence of temperature await further experimental data. The results obtained by different analysts for the same leather under apparently the same conditions show that much greater precision is required in work of this kind. That the smallness of the sample used is responsible for some of the trouble is doubtful; Kern had no difficulty at all in checking his results any number of times, but his results did not check those of other members.

I must take issue with Mr. Schultz on the question of the probability of the completeness of saturation of the collagen by tannin in any of the Committee leathers. I have yet to find a piece of leather that is not much more heavily tanned in the grain and flesh layers than in the middle layer. In fact, if the leather is split into five or more layers, each will be found to have a different degree of tannage. As for his figures dealing with the so-called "purity" of the water-soluble matter, I hold that they are

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meaningless, having been obtained by an incorrect method of tannin analysis.

What is apparently needed is not further collaborative work so much as a thorough study of the problem under conditions of the greatest possible refinement.

TABLE I.

LEATHER SAMPLE No. 1.—Analysis of leather, as received, showed: water 9.72 per cent. (Porter), 14.54 per cent. (Kern), and fat 4.63 per cent. (Porter), 4.62 per cent. (Kern). Eight grams leather were extracted with petrol to remove fat, air-dried to remove solvent, and then shaken for 1 hour each with successive 100 cubic centimeter portions of water. These were collected, each liter of extract was kept separate and the dry residue of an aliquot weighed.

	By R. E. Porter. Temperature of water when added to leather			By E. J. Kern.		
	30°	50°	95°	30°	50°	95°
Liter No.	Grams residue in 100 cc. of extract					
1	0.1794	0.1820	0.1556	0.2054	0.2078	0.2025
2	0.0255	0.0245	0.0175	0.0213	0.0210	0.0142
3	0.0175	0.0165	0.0125	0.0120	0.0119	0.0060
4	0.0160	0.0130	0.0080	0.0073	0.0078	0.0022
5	0.0125	0.0115	0.0075	0.0052	0.0053	0.0019
6	0.0109	0.0095	0.0060	0.0045	0.0047	0.0014
7	0.0113	0.0100	0.0077	0.0034	0.0034	0.0006
8	0.0085	0.0085	0.0057	0.0017	0.0030	0.0006
9	0.0057	0.0070	0.0037	0.0012	0.0016	0.0000
10	0.0060	0.0065	0.0030	0.0017	0.0016	0.0000
Total residue of 10 liters	2.933	2.890	2.272	2.637	2.681	2.294
Equals per cent. absolutely dry leather	40.61	40.02	31.46	38.57	39.21	33.55

By the Official Method Porter found 30.94 parts water-soluble per 100 of absolutely dry leather, using a 30-gram sample not extracted with petrol, and 30.58 parts water-soluble, using an 8-gram sample after extraction with petrol.

TABLE II.

LEATHER SAMPLE No. 2.—Analysis of leather, as received, showed: water 13.40 per cent. (Schultz), 13.52 per cent. (Kern), and fat 1.10 per cent. (Schultz), 1.12 per cent. (Kern). Eight grams leather were extracted with petrol to remove fat, air-dried to remove solvent, and then shaken for 1 hour each with successive 100 cubic centimeter portions of water. These were collected, each liter of extract was kept separate and the dry residue of an aliquot weighed.

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	By G. W. Schultz. Temperature of water when added to leather			By E. J. Kern.		
	25°	50°	95°	30°	0°	95°
Liter No.	Grams residue in 100 cc. of extract					
1	0.2130	0.2194	0.2108	0.2228	0.2229	0.2124
2	0.0197	0.0198	0.0170	0.0222	0.0198	0.0131
3	0.0167	0.0150	0.0110	0.0132	0.0122	0.0046
4	0.0140	0.0112	0.0094	0.0089	0.0077	0.0034
5	0.0120	0.0103	0.0098	0.0064	0.0049	0.0010
6	0.0079	0.0058	0.0038	0.0052	0.0039	0.0015
7	0.0058	0.0067	0.0054	0.0042	0.0026	0.0009
8	0.0082	0.0068	0.0062	0.0030	0.0010	0.0000
9	0.0094	0.0075	0.0066	0.0024	0.0016	0.0000
10	0.0082	0.0065	0.0056	0.0016	0.0012	0.0000
Total residue of 10 liters	3.149	3.090	2.856	2.899	2.778	2.369
Equals per cent. original leather	39.36	38.63	35.70	36.24	34.73	29.61
Total residue of 15 liters	3.450	——	——	——	——	——
Equals per cent. original leather	43.12	——	——	——	——	——

Using a 30-gram degreased sample, Schultz found 29.14 per cent. water-soluble by the Official Method.

TABLE III.

LEATHER SAMPLE No. 3.—Analysis of leather, as received, showed: water 8.37 per cent., fat 8.14 per cent. Eight grams leather were extracted with petrol to remove fat, air-dried to remove solvent, and then shaken for 1 hour each with successive 100 cubic centimeter portions of water. These were collected, each liter of extract kept separate and the dry residue of an aliquot weighed.

	By Paul Hayes. Temperature of water when added to leather		
	30°	50°	95°
Liter No.	Grams residue in 100 cc. of extract		
1	0.0869	0.0880	0.0781
2	0.0251	0.0238	0.0197
3	0.0162	0.0131	0.0105
4	0.0116	0.0106	0.0075
5	0.0111	0.0095	0.0055
6	0.0075	0.0075	0.0041
7	0.0078	0.0058	0.0037
8	0.0097	0.0055	0.0031
9	0.0066	0.0044	0.0018
10	0.0034	0.0027	0.0016
Total residue of 10 liters	1.859	1.709	1.356
Equals per cent. original leather	23.24	21.36	16.95

Found by the Official Method 15.56 per cent. water-soluble; 12.93 per cent. in the first liter of extract and 2.63 per cent. in the second. In the above extractions, after 2 liters had been extracted, no further extract gave a test for tannin with the gelatin-salt reagent.

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TABLE IV.

LEATHER SAMPLE No. 2.—Figures show total per cent. matter extracted from 8 grams of leather, obtained by weighing dry residues of extracts. Work done by G. W. Schultz.

Total No. of washings	Cubic centimeters water at room temperature used for each washing				
	100	200	300	400	500
	Shaking Each for 15 Minutes				
1	15.59	17.56	18.58	19.03	19.03
2	19.20	20.96	21.83	21.89	22.16
3	21.16	22.58	23.47	23.08	23.80
4	22.20	23.62	24.67	24.30	25.16
5	22.98	24.51	25.71	25.37	26.26
6	23.72	25.36	26.46	26.32	27.03
7	24.41	26.08	27.27	26.96	27.62
8	24.94	26.71	28.08	27.75	28.20
9	25.43	27.24	28.78	28.51	29.00
10	25.79	27.72	29.43	29.10	29.60
	Shaking Each for 1 Hour				
1	16.54	18.64	20.38	20.84	20.93
2	20.51	22.26	23.84	24.23	23.97
3	22.31	23.92	25.73	26.22	25.29
4	23.47	25.25	27.03	27.53	26.31
5	24.30	26.30	27.99	28.47	27.32
6	25.13	27.11	28.76	29.31	28.07
7	25.74	27.75	29.46	30.04	28.67
8	26.19	28.27	30.09	30.77	29.20
9	26.65	28.76	30.71	31.43	29.69
10	27.09	29.17	31.35	32.02	30.22
	Shaking Each for 5 Hours				
1	17.35	19.45	20.98	21.42	21.63
2	21.12	23.07	24.75	24.93	25.16
3	22.87	24.79	26.70	27.07	27.10
4	24.09	26.05	28.01	28.37	28.52
5	25.04	27.04	29.09	29.47	29.68
6	25.83	27.83	30.08	30.38	30.68
7	26.53	28.49	30.88	31.17	31.67
8	27.16	29.13	31.55	31.79	32.40
9	27.64	29.73	32.06	32.33	33.04
10	28.09	30.24	32.58	32.84	33.63

TABLE V.

LEATHER SAMPLE No. 2.—Figures show total per cent. matter extracted from 8 grams of leather, obtained by weighing dry residues of extracts, using 500 cubic centimeters water at 50° C. for each washing. Work done by G. W. Schultz.

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Total No. of washings	Shaking each for 15 min.	Shaking each for 30 min.
1	22.58	25.07
2	26.96	29.26
3	29.28	31.01
4	30.62	32.23
5	31.69	33.11
6	32.45	33.90
7	33.11	34.68
8	33.75	35.27
9	34.24	35.86
10	34.68	36.68
11	35.14	37.24
12	35.71	37.73
13	36.14	37.90
14	36.50	38.16
15	36.79	38.40
16	37.21	38.73
17	37.61	39.07
18	38.01	39.45
19	38.39	39.99
20	38.55	40.39

TABLE VI.

LEATHER SAMPLE No. 3.—Figures show total per cent. matter extracted from 8 grams of leather, obtained by weighing dry residues of extracts. Work done by Paul Hayes.

Total No. of liters of extract	Shaking with 200 cc. portions of water at 50° C. for 1 hour each	In Teas Extractor with water at 85° to 90°
1	10.91	15.41
2	13.41	17.09
3	15.46	18.41
4	17.07	19.43
5	18.18	20.44
6	19.09	21.51
7	19.89	22.29
8	20.73	22.93
9	21.45	27.83*
10	22.00	29.18*
11	22.60	——
12	23.30	——
13	23.85	——
14	24.20	——
15	24.66	——
16	25.06	——
17	25.38	——

* The 9th and 10th liters were obtained by reflux condensation for 24 hours each.

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TABLE VII.

LEATHER SAMPLE No. 2.—Eight grams of leather were extracted by percolation with water at 25° C. at the rate of 2 liters per 3 hours. Figures show total matter extracted as per cent. of original leather. Work done by G. W. Schultz.

Total No. liters of extract	A	B	C	D	E	F
2	27.28	25.95	25.67	26.60	23.68	26.15
4	29.74	27.92	28.08	28.63	25.43	28.45
6	31.29	29.45	30.42	30.08	26.71	29.90
8	32.59	30.77	31.51	31.30	27.91	31.12
10	33.39	31.58	32.16	32.06	28.63	31.80
12	34.42	32.67	32.99	32.99	29.55	32.75
14	——	——	33.70	33.54	29.99	33.62
16	——	——	34.02	33.82	30.21	33.92
18	——	——	34.39	34.12	30.53	34.38
20	——	——	34.50	34.21	30.75	34.55
Calculated from loss in weight of leather extracted with 12 liters of water	32.18	31.08	——	——	——	——
Calculated from loss in weight of leather extracted with 20 liters of water	——	——	33.05	33.48	——	——
Calculated from loss in weight of leather extracted with 60 liters of water	——	——	——	——	34.35	35.36

TABLE VIII.

LEATHER SAMPLE No. 2.—Same procedure as noted in Table VII, excepting that water at 50° C. was used. Work done by G. W. Schultz.

Total No. liters of extract	A	B	C	D	E	F
2	32.23	32.80	31.88	31.95	32.68	32.68
4	34.28	35.13	33.88	33.53	34.88	34.38
6	35.82	36.56	35.34	34.93	36.27	35.87
8	——	——	——	35.98	37.34	36.93
10	——	——	——	36.71	38.04	37.70
12	——	——	——	37.24	38.60	38.27
14	——	——	——	37.74	38.99	38.71
16	——	——	——	38.17	39.41	39.22
18	——	——	——	38.68	39.95	39.78
20	——	——	——	39.23	40.42	40.35
22	——	——	——	39.84	40.90	40.75
24	——	——	——	40.33	41.41	41.13
26	——	——	——	40.80	41.87	41.55
28	——	——	——	41.29	42.45	41.84
30	——	——	——	41.67	42.91	42.41
32	——	——	——	42.28	43.46	42.96
34	——	——	——	42.79	43.99	43.46
36	——	——	——	43.07	44.16	43.68
38	——	——	——	43.34	44.49	43.92
40	——	——	——	43.61	44.73	44.10
Calculated from loss in weight of leather extracted with 6 liters of water	35.56	35.31	34.80	——	——	——
Calculated from loss in weight of leather extracted with 40 liters of water	——	——	——	41.54	——	——
Calculated from loss in weight of leather extracted with 60 liters of water	——	——	——	——	42.17	42.26

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TABLE IX.

LEATHER SAMPLE No. 3.—Eight grams of leather were extracted by percolation with water at 20° C. at the rate of 1 liter per hour. Figures show total matter extracted as per cent. of original leather. Work done by Paul Hayes.

Total No. liters of extract	Matter extracted
2	8.33
4	10.61
6	12.26
8	13.38
10	14.41
12	15.23
14	15.76
16	16.38
18	16.89
20	17.45
22	17.86
24	18.20
26	18.73
28	19.15
30	19.60
Calculated from loss in weight of leather extracted with 30 liters of water	18.40
Calculated from loss in weight of leather extracted with 60 liters of water	25.16

TABLE X.

LEATHER SAMPLE No. 4.—Analysis of leather, as received, showed: water 10.50 per cent. (Porter), 11.93 per cent. (Kern), and fat 4.78 per cent. (Porter), 4.62 per cent. (Kern). Eight grams of leather were extracted by percolation with water at temperatures noted. Figures show total matter extracted as per cent. of original leather. Work done by R. E. Porter.

Total No. liters of extract	At 30°		At 50°	
	A	B	A	B
2	28.11	27.00	30.00	30.00
4	31.99	30.25	32.62	32.92
6	34.54	33.00	34.55	34.85
8	36.16	34.50	36.12	36.30
10	37.58	36.00	36.95	37.18
12	38.78	37.25	37.85	37.98
14	39.80	38.08	38.68	38.80
16	40.43	38.66	39.06	39.30
18	41.18	39.16	39.81	40.10
20	41.48	39.51	40.19	40.80
22	41.98	40.06	40.71	41.13
24	——	——	41.01	41.19
Average	41.02		41.10	
Calculated from loss in weight of leather extracted with 24 liters of water	40.38		40.75	
Calculated from loss in weight of leather extracted with 48 liters of water	40.75		42.88	

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TABLE XI.

LEATHER SAMPLES No. 2, No 3, AND No. 4.—Eight grams of leather were extracted by percolation with water at 25° C. The water was passed over the leather at the rate of about 2 liters per 3 hours, although this rate was somewhat increased for each duplicate to determine its effect, if any, upon the end-point. Figures show total matter extracted as per cent. of original leather. Work done by E. J. Kern.

Total No. liters of extract	Leather No. 2		Leather No. 3		Leather No. 4	
	A	B	A	B	A	B
2	27.66	27.02	9.72	9.34	24.05	21.91
4	28.77	27.64	10.62	10.61	24.75	23.01
6	30.46	28.73	12.14	11.56	25.77	25.28
8	30.97	30.46	12.54	12.24	26.49	25.99
10	31.75	31.39	13.12	12.66	27.16	26.74
12	32.04	32.15	13.55	13.23	27.73	27.36
14	32.35	32.64	13.63	13.35	28.16	27.83
16	32.39	32.75	14.20	14.05	28.36	28.05
18	33.12	33.37	14.67	14.87	28.53	28.33
20	33.99	33.95	15.10	15.37	28.90	28.61
22	34.48	34.55	15.33	15.64	29.17	28.86
24	34.84	34.95	15.55	15.91	29.44	29.13
26	34.95	35.15	15.70	16.03	29.56	29.30
Average for 26 liters.....	35.10		15.87		29.43	
Calculated from loss in weight of leather extd. with 26 liters of water	35.33		16.40		29.97	
Calculated from loss in weight of leather extd. with 52 liters of water	35.29		16.53		29.89	

THE COLOR MEASUREMENT OF VEGETABLE TANNING SOLUTIONS.

Committee Report.

By T. Blackadder, Chairman.

The work of this committee was suggested by a paper published in this JOURNAL by Blackadder and Garland.[1] They had approached the subject of color measurement of solutions from the standpoint that it ought to be possible by applying purely physical considerations to develop a sufficiently exact and reliable measurement of the color of tanning solutions with a standard machine suitable for the average tanning laboratory. They indicated a first step to be taken in a suggestion that the Hess-Ives

[1] **15**, 181 (1920).

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Tint Photometer made color measurements on a more theoretically correct basis than the Lovibond machine or any of its modifications which are at present used.

On account of the necessity of special apparatus and the nature of the problem in its present stage, the work was not well fitted for committee work, and this year's work was carried out in the Chairman's laboratory.

The first step taken was to subject the Hess-Ives Tint Photometer to a rigid test. A description of this machine and the principle upon which it is based was given in this JOURNAL.[1] The first point investigated was the reliability of the machine using different illuminants. Colors were read using the ordinary clear electric bulb at a low voltage, and repeating the measurements with a daylight bulb at normal voltage, giving great extremes in the illumination. The figures obtained were almost identical in both cases. Typical figures are shown in Table I. The second

TABLE I.—EFFECT OF VARIATION OF ILLUMINANT.

Solution of extract Analytical strength	Readings Red	Green	Blue	Illuminant
Chestnut wood	54	20	3	Clear bulb (Yellowish light)
Chestnut wood	53½	20	3	Blue bulb (White light)
Oak bark	55	15½	1½	Clear bulb (Yellowish light)
Oak bark	55	15½	1½	Blue bulb (White light)

point investigated was the difference between different operators' eyes. In this test the machine gave very good concordance between different operators. The third point investigated was the power of differentiating between solutions. On this point the machine appeared weak. It appeared that if an extract solution had iron added to it in successive amounts the effect was a gradual lowering of all three color readings. (See Table II.) This reaction of the color to the iron is surprising to those who have had experience with the quick rise in the blue reading of a Lovibond machine caused by the addition of iron. To begin with, it mislead us and we cast around for a fault in the machine. We found that without a doubt the machine had a fault in that the blue reading was caused entirely by the blue filter letting through a narrow band of red light. This fault, however, can be obviated by neglecting the blue reading or by use of a different set of

[1] *L. c.*

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color screens. Most important, however, are the findings we made by use of the spectroscope while locating this fault. It appeared that no extract we examined passed any blue light whatsoever, in a solution of analytical strength. The significance of this lies in that our color scale needs no blue reading for these extracts and the use of a blue reading is erroneous and misleading. We believe that any use of the blue in our standard is wrong, and would suggest that red, yellow and green would cover the necessary range of colors.

TABLE II.—EFFECT OF ADDITION OF IRON TO EXTRACT OF CHESTNUT WOOD.

Amount of iron added	Readings			Illuminant
	Red	Green	Blue	
None	56	23½	3½	Blue bulb
0.0025%	52½	20½	3	Blue bulb
0.0050%	51¾	20	2¼	Blue bulb
0.0100%	46	17¼	2	Blue bulb
0.0150%	41¼	15¼	1¾	Blue bulb
0.0200%	35½	13	1¼	Blue bulb

This findings has its bearing on the use of blue in the Lovibond scale. We believe that the use of a blue in any combination of color to match a tanning solution is unnecessary and if used is liable to lead to error.

Further than this we have not gone at present. We have tried to make photographs of the spectrum thrown by the various solutions of extracts to include with this report, but our apparatus did not suffice. We believe that these photographs would be advantageous in selecting suitable color standards, and suggest securing these photographs as a next step.

A criticism which applies to all methods of color measurement made on solutions is that which asks what reason have we for believing that a filtered solution is at all comparable in color to the original solution with reds present. This critcism is not of absolute importance because the color of the filtered solution has its value as a standard to-day, and we are at present mainly interested in a reliable measure of this standard. While it is obviously impossible to give a definite answer to the above criticism, we can make the attempt to learn whether the presence of reds makes a definite change in the color of the leather tanned with the two solutions, and this to our mind, is practically a sufficient answer. We have, therefore, experimented with chestnut wood, hemlock

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and oak bark, and ordinary quebracho extracts by tanning skivers of cowhide grain splits with water solutions of the extracts before and after filtering, and did not find any appreciable difference resulting from the filtration. It would appear that the color of the solution is therefore equivalent to the skivers as far as this criticism is concerned.

In the opinion of the chairman the determination of the color of tanning solutions by a colorimeter is of value to tanner and extract manufacturer. The disfavor under which these determinations at present labor is in great measure due to the limitations of the apparatus at present used. An apparatus which is based on matching a built up color standard against the unknown color will not prove satisfactory, but a machine based on spectrum analysis ought to be capable of adaptation to our needs.

The Chairman recommends the continuance of this Committee to carry on this line of work. He also asks for discussion and criticism from the Association at large, for in its present stage, the work is unavoidably confined to one laboratory and may easily suffer from being too one-sided.

BOOK NOTICE.

MODERNE GERBMETHODEN (Modern Methods of Tanning). By Ing. Josef Jettmar. Second Edition, completely rewritten and enlarged. 264 pages with 19 cuts. A. Hartleben's Verlag, Vienna and Leipzig, price 24 marks plus 20 per cent.

A brief but very comprehensive work that contains much of value to both leather chemists and practical tanners. Those who read German will truly find many practical hints and instructions in this book. In it some of the essential adjunct operations of modern tanning are treated in the light of advances made in science during the last two decades, such as, the use of sharpened soaks, unhairing, deliming with acids, artificial bates, stuffing with the use of soap liquor, bleaching of vegetable tanned leather and the bleaching of tawed and chamois leather. The production of unusual and rarer kinds of leather, such as, transparent and picric acid leather, sulphur leather, etc., are treated of as well as the modern methods of producing a variety of well known kinds of leather, such as, drum tanned sole leather, semi-chrome from calf-skins and East India sheep and goatskins, combination tanned kips, colored chrome calf, various furniture leathers, mocha leather, patent chrome and others as well as the working up of flesh splits, offal and the preparation of leather lacquers.

In the preface to the first edition the author stated that this work was compiled with the twofold object of acquainting the tanner who is less

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familiar with the technical literature of some new processes in the production of pelts, their tanning and finishing, in such a way that he may see how and why this or that is done. Also that it may be made clear to him that tanning in the past two decades has ceased to be a mechanical handicraft as frequently practiced even in the latter part of the last century. Leather making has grown to be an industry conducted by machinery and requires very much and superior knowledge. The modern tanner must command a rather extensive knowledge of physics, chemistry and mechanics in order to keep pace with the progress of his industry, and it was hoped that this book would at least fill up some of the gaps in his knowledge and point the direction in which he should extend it.

ABSTRACTS.

Method for Expressing the Basicity of Chrome Liquors. By K. SCHORLEMMER, *Coll.*, **607**, 536-8 (1920). A review of previous methods has been given by Procter (*J. S. L. T. C.*, **2**, 259 (1918), and Blockey (*J. S. L. T. C.*, **3**, 11 (1919). By the author's method the total chrome content (expressed in per cent. Cr_2O_3) of a chrome liquor is determined by oxidation with hydrogen peroxide, and titration with sodium thiosulphate after adding potassium iodide. Another portion of the liquor is titrated hot with N/2 sodium hydroxide solution as for acid, but instead of calculating for acid radicle a calculation is made of the percentage of Cr_2O_3 which precipitates, that is, the percentage of Cr_2O_3 bound to acid groups other than hydroxyl by multiplying the number of cc. of N/2 NaOH required by 0.012683. The percentage which this is of the total chrome content is calculated, and subtracted from 100, giving the percentage of the total chrome which is bound to hydroxyl groups. This is the "basicity" of the liquor. For example, the basicity of $CrOH(SO_4)$ is 33⅓ per cent. and of $Cr_2(OH)_2Cl_2$, 50 per cent. The result by this method is the same no matter whether the salt is a chloride, sulphate or a mixture or whether the chrome content is expressed as Cr_2O_3 or as Cr. It can also be used for aluminum salts. I. D. C.

The Swelling of Dehaired Skins. By G. GRASSER, *Coll.*, **604**, 353-59; **605**, 405-16; **606**, 456-64; **607**, 512-20 (1920). The author reviews and discusses the work on the swelling of gelatine and skins by the following: Vilhelmy, *Pogg. Annalen*, **119**, 121-2; Paessler and Appelius, *Coll.*, 1902, 22 and 179; Stiasny, *Coll.*, 1909, 302 and 373; Hough, *Leather*, 1912, 63; Von Schroder, *Coll.*, 1902, 306, 1903, 177 and 201; Zacharias, *Zeit. fur phys. Chem.*, 1902, **39**, 468; Procter, *Leather World*, 1913, 15 and 273; *Coll.*, 1914, **528**, 194; *Kolloid Chem. Beihefte*, 1911, 243; Powarnin, *Coll.*, 1914, **533**, 659; Morse and Pierce, *Zeit. phys. chem.*, 1903, **45**, 568. Instead of gelatine or hide powder Grasser, in his work, used small strips of unhaired skins. These were completely delimed with boric acid, preserved in 1 per cent. phenol and ½ per cent. mercuric chloride, and washed just before using in distilled water. In the first experiment more acid was

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found to be absorbed where the grain side only was exposed to the acid than when the flesh side only was exposed. When the pieces were immersed in the acid an intermediate amount of acid was absorbed. This acid was all recovered when the pieces were left for eight hours in N/10 potassium hydroxide. In the remaining work the pieces were immersed in the acid for a given time, then removed, rinsed, dried by pressing lightly between cloths and weighed. The acid was then titrated. By varying the time, using pieces weighing 2 grams and 18 cc. of water containing 1.98 cc. normal hydrochloric acid, a maximum swelling and also a maximum absorption of acid was reached in 2 hours. This absorption remained constant for 4 hours and then decreased as the time was further increased. When the concentration of acid and the time were kept constant and the size of the pieces varied, the larger pieces absorbed more acid, but the relative swelling was the same (52 per cent.). As the concentration of the acid was increased the amount of acid absorbed increased regularly, but the swelling reached a maximum at a concentration of 1.01 cc. normal hydrochloric acid in 20 cc. With 2-gram pieces of skin, 20 cc. of solution and 2 hours time, there was a depleting action if the concentration of acid was less than 0.4 cc. of normal hydrochloric, but with greater amounts of acid there was a swelling action. The influence of the anion and of the cation was investigated by adding varying amounts of different salts to 1.98 cc. normal hydrochloric acid in 18 cc. of water and using 2 grams of skin. A constant amount of acid (1.15 cc.) was absorbed in every case indicating that there was a chemical reaction between the acid and hide substance. Varying amounts of the various salts were absorbed and the swelling was decreased in all cases. Further experiments with salts of the various metals and acids showed that the anion had no influence, but there was some similarity between the effect of the metals of certain groups. Further experiments were conducted with acetic, monochloracetic, lactic, oxalic and formic acids. First the concentration was determined at which maximum swelling occurred and then the minimum time required for maximum swelling.

Acid	Acetic	Monochloracetic	Formic	Lactic	Oxalic
No. of hours required to reach max. swelling....	3	4	6	2½	2
Cc. of normal acid required to produce max. swelling	7.42	1.5	2.67	2.50	2.10

Using this optimum concentration of acid and time, the influence of various salts on the absorption was investigated. Sulphates had a great depleting action and the effect at low concentration was much greater than with salts of other acids. The depleting action of nitrates and chlorides was approximately proportional to the concentration of salt present, but nitrates had a greater effect than chlorides. The neutral sodium salt of the acid in question had an effect almost similar to that of chlorides. The cause of the depleting action of salts could not be determined. It was

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not due to osmotic pressure for the depletion was not proportional to the concentration and also the final depletion was not great enough. An experiment with beet sugar showed that sugar has a slight swelling rather than a depleting action. The degree of dissociation of the acid did not influence the velocity of swelling appreciably since these were not proportional. In all cases 2 grams of hide absorbed approximately 1.15 cc. normal acid. One hundred grams of dry hide substance would therefore absorb 139 cc. of normal acid or 5 grams of hydrochloric acid. Using the formula $C_{35}H_{57}O_{13}N_{11}$ for hide substance 1 gram molecular weight would absorb 42 grams of hydrochloric acid. This is quite near 36, the amount which would be absorbed if a compound was formed having the formula $C_{35}H_{57}O_{13}N_{11}.HCl$. I. D. C.

The Mission of a Research Institute for the Leather Industry. By E. STIASNY, *Coll.*, **606**, 449-56 (1920). An address discussing the value of an institute for theoretical research in addition to institutes for technical or practical research. As an example of the difference in the work which the two laboratories would perform, in studying fat liquors the latter would investigate the stability of emulsions of various substances, the action of these emulsions on leather and chemical methods for controlling their production and use, while the former would study the properties of the fats, the size of the particles in emulsions, the relation between the size of the particles and surface tension, and the interfacial tension between various liquids. I. D. C.

Some Notes on One-Bath Chrome Tanning and on Determining the Tanning Strength by the Agglutination Method. By E. STIASNY, *Coll.*, **606**, 479-85 (1920). Stiasny and Burger found that bated skins, when placed in a chrome liquor, took up the two hydrolytic products separately. The acid was taken up quickly and reversibly and the chrome salt slowly and irreversibly. Griliches (*Zeit. fur Elektrochemie*, **26**, 342, 1920) did not find this initial absorption of acid, but in his work he used a strongly basic liquor and skins which had been pickled with acid. Both of these would decrease the acid absorption and hasten the absorption of the chrome salt. If Griliches had made tests after 1, 2, and 5 minutes instead of after 15 minutes he might have found an initial acid absorption. The possible error in his work was also great.

Kobert (*Coll.*, 1917, 201), by the agglutination method, found no difference in the tanning properties of violet and green chromium salts, but before using them the salts were almost neutralized and it is well known that this changes the character of the salts. Neither is the agglutination method suitable for this work. It indicates, for example, that substances such as copper or lead acetates have a high tanning value when this is not the case. I. D. C.

Production of Imitation Crocodile Leather. *Neueste Erfindungen und Erfahrungen*, 1919, 423; through *Coll.*, **606**, 489 (1920). Sheepskins are ordinarily used, but goat or calfskins are used if very durable leather is

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desired. The design may be obtained by using either a press or an embossing machine. The latter is suitable only for small designs; and should be used with the rolls hot. The skins must be dried on frames after embossing to prevent warping. Pressing is most conveniently done in a hydraulic press with a plate large enough to accommodate a whole skin. The skins must not be so thin or damp that they will cut through in places. Dye should be applied immediately after pressing and should be applied carefully so that it does not get into the wrinkles. The skins are dried, then glazed by machine, coating if necessary before glazing with a mixture of 10 volume of water and 1 volume of milk. I. D. C.

Retention and Determination of Free Sulphuric Acid in Leather. By W. MOELLER, *Coll,* **606**, 465-70 (1920). Moeller states that there is little foundation for Immerheiser's theory that sulphuric acid reacts at once even in dilute solution with hide or leather, but that there is a reaction and loss of acid after the acid has become concentrated during analysis. The low adsorption of acid by leather which Immerheiser found it due first to the fact that the coating of tannin hinders the penetration and adsorption of acid and also to the fact that although the tannin does not absorb acid, Immerheiser's calculations are based on the weight of leather instead of the actual hide substance. I. D. C.

Tanning Materials of Our Colonies (French). By H. JUMELLE, *Chimie et Industrie,* **5**, 103-8 (1921). A brief review of recognized and of possible new sources of tanning materials in Algeria, Tunisia, Morocco, occidental and equatorial Africa, Madagascar and Indo-China. Among the newer tanning materials of Morocco is *takaout,* a gall from the flowers of *tlaia* or *Tamarix articulata.* The galls average about 40 per cent. tannin and in powdered form are used for the tannage of the finest sheep and goatskins. Of the many varieties of *Acacia arabica* in occidental French Africa, two especially deserve consideration. They are *tomentosa,* which is the *neb-neb* of Onolofs and *Adansoni* or *gonakié.* The pods of *neb-neb* contain from 30 to 40 per cent. tannin and the bark about 10 per cent. Considerable laboratory work has been done by Heim, Matrod, and Maben (see Abstract, this JOUR., **16**, 290) on *gonakié* from which it has been concluded that it can replace Sicilian sumac to a large extent. With the seeds the shells of *gonakié* gave 25 per cent. tannin while without the seeds they gave from 35 to 40 per cent. tannin. The entire *gonakié* shells do not give as good a color as do those from which the seeds have been removed and the fresh shells from the point of view of color are preferable to the old ones. In Madagascar and Indo-China the most important materials are the numerous varieties of mangrove and black wattle. Madagascar alone has an estimated area of more than 800,000 acres which if properly handled represents an inexhaustible supply. The botanical names, the native terms, and the tannin content of many varieties of tanning materials of the French colonies are given. R. W. F.

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Scientific Organization for Glue Works. By V. CAMBON, *Chimie et Industrie,* **5,** 96-102 (1921). In an appeal for modernizing the industries of France a detailed description of an up-to-date, properly equipped, and logically arranged glue works is given to show the advantages thereby possible. A detailed sketch of such a plant with a daily capacity of 10,000 kg. of bone is given and the raw material is followed through its entire course. In the arrangement and equipment the following general principles are observed: the distribution of the workmen so that the operations can be carried out in a logical order and under conditions to facilitate supervision; reduction to a minimum of transportation by man power and of hand labor; economy in fuel by proper relative location of generators and by insulation; complete recovery of by-products; and allowance for increase in capacity without disarranging existing buildings and equipment. On the basis of 10,000 kg. of bone per day for 360 days per year the author figures a saving over the usual out-of-date factories of 90,000 francs for labor; of 200,000 francs through the greater yield of grease by petroleum ether degreasing of the bones instead of by warm water; of 50,000 francs by recovery of residues from cleaning the bones; and of 100,000 francs through more economical utilization of fuel. R. W. F.

Clarification and Solubilization of Tanning Extracts. By GEORGES VIE, *Le Cuir,* **10,** 36-38 (1921). Clarification, solubilization, and decoloration all have for their object the removal of insolubles in extracts either by precipitation or solution. Decoloration generally involves precipitation with an appreciable loss in tannin so that extracts simply clarified are richer in tannin. Decolorizing by blood is not only a wasteful practice, but does not justify the expense. The assertion of certain tanners that blood decolorized chestnut extract gives a greater yield than clarified extract is questioned. Conclusions for heavy leathers cannot be drawn from results with small skins. It is believed that the tanner would find it economical to use the cheaper and richer clarified extracts.

Instead of the usual sulphite or bisulphite clarification of quebracho the Badische Anilin und Soda Fabrik patented before the war a process for the treatment of difficultly soluble extracts to make them completely soluble in cold water which consists of treating the extract with a compound of formaldehyde and phenols or phenol sulphonic acids with or without condensation agents (French Patent 443,750, English Patent 24,982). By this procedure to 500 kg. of quebracho extract of 18° to 21½° are added 100 liters of water containing 200 kg. of sodium salt produced by the condensation of formaldehyde and cresol sulphonic acid as described in the patent. The same method could be applied to other vegetable extracts such as mangrove and chestnut. The above procedure offers one of the principal uses for the synthetic tannins and is surprisingly little known when one considers the advantages therefrom.

Insolubles are divided into two classes: those from a transformation of the tannin and those from inorganic salts and heavy metals. The last, while insoluble in water, have undisputed tanning properties. The me-

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chanical absorption of insoluble powders and their tanning action show that the complete solubility in the cold demanded to-day of extracts is not indispensable. The tanning action of phlobaphenes and their partial solubilization during tannage is admitted. In the long time tannage of heavy leathers certain qualities of firmness, yield, and water resistance are obtained in part by deposition of insoluble ellagic and phlobaphene materials, which effect it would seem reasonable to suppose, could be obtained by milling with incompletely soluble extracts giving a mechanical absorption of the insolubles. In the solubilization of extracts containing reds, weak alkalies, carbonates, and particularly sulphites and bisulphites are used. Many of the quebracho extracts have been rendered completely soluble by use of either of the last two. Sulphited extracts also give a fairer colored leather. While the question of color for upper and light leathers is important, it is absolutely absurd for sole leather. Sulphited extracts, being somewhat antiseptic require the addition during tannage of artificial acids. Apparently one of the best procedures for clarifying chestnut extract is the use of borax to the extent of 4 to 5 per cent., although it has the disadvantage of requiring a large quantity of water for solution before adding to the extract. Chestnut extract thus treated gives a fairer color on sheepskins than does the pure extract.

R. W. F.

Hogskins in the Tannery. By GEORGES VIE, *Le Cuir,* **10**, 59-61 (1921). Hogskins are particularly suited for saddlery. Only fine grained ones are selected. Thorough soaking and preliminary working must be done to remove the large quantities of grease so that stains and irregular and incomplete tannage can be avoided. The bristles are readily removed after a few hours in sodium sulphide or 20 to 24 hours in old limes. The skins are then worked on the beam and put into new limes. Liming should not be hastened and will require about 15 days with strengthening of the limes and working of the skins on the beam every 48 hours. Because of the irregularities of the skins fleshing requires extreme care and skill. Bating or puering is best done in two baths; first in an old puering bath for 24 hours, then a working upon the grain and then into a bath containing about 500 gms. of dung for each skin of medium size. After about 24 hours in the fresh puer if the skins are sufficiently fallen they are worked on the grain, put into clear water for 10 to 12 hours and then drained. Oak tannage is to be preferred, although chestnut is sometimes used. To obtain a slight plumping it is best to begin with sulphite cellulose or pine liquors. Some tanners recommend gambier and quebracho followed by sumac to brighten up. Commercially the skins after treatment with gambier, which possesses certain advantages from the standpoint of suppleness and plumping, are put in oak bark for about 1 month and then finished with quebracho, the latter being added to the pits already containing the gambier and oak bark. The complete tannage requires about 4 months. The skins are then thoroughly washed, bleached if necessary, and washed again, set out, fluffed, retanned for 3 days in a bath of warm quebracho containing

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4 liters of ordinary extract per dozen skins, then thoroughly washed and drained. After partially drying stuffing is done with a mixture of 2 parts talc, 2 parts of melted yellow wax and 6 parts linseed oil. Upon drying the wax remains on the surface and can be polished to a bright finish. The flesh side is dressed with a mixture of cod and tallow and finally, if desired, the leather is glazed with albumen. Dyeing may be done in the usual manner with logwood, fustic, iron and potassium dichromate or with artificial dyes. A finish of gelatine and linseed gives good results.

R. W. F.

Gonakié Husks of Senegal. By F. HEIM, *Halle aux Cuirs,* Feb. 20, 1921, 54-8. Tanning experiments with gonakié and mixtures of the same with sumac and quebracho respectively on sheep, goat, and calfskins gave entirely satisfactory results. A commercially made extract from the entire husk showed: tannin 24.6; non-tannin 18.2; insolubles 1.2; moisture 55.7; ash 2.32; density 1.211; and gave a Lovibond color reading of 3.8 red and 8.0 yellow. Commercial extraction should be made similar to that for sumac, the seeds which the shells contain are useless for tannin and should be removed. It is concluded that gonakié would warrant regular exploitation and with the seed removed and decolorized it can replace Sicilian sumac to a large extent. R. W. F.

Tannin from the Viewpoint of Biological Chemistry. ANONYMOUS, *Halle aux Cuirs,* Feb. 20, 1921, 33-44. Tannin appears to be a non-assimilated product of vegetable life, an excretion analogous to animal excretions; a poison which is eliminated from the vital circulation and prevented from returning thereto by cyclization. According to Pictet the toxic products of non-assimilation are converted into closed chain or cyclic compounds so as to prevent their passage through the plant cells or ducts thereby rendering them harmless to the plant life. The galls would appear to be vegetable tumors formed by a reaction of the living organisms provoked by the presence in their tissue of some foreign body such as an egg or parasite. This reaction leads in the animal organisms to the development of an embryo or sometimes of a malignant tumor and in the vegetable organisms to the production of fruit or sometimes to a gall or parasitic tumor. Tannin, due to its acid and coagulating nature, plays an important role in artificial fecundation by the method of Delage which is based on successive coagulation and liquifaction of the colloidal matter. R. W. F.

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G. W. SCHULTZ . . . . . Associate Editor

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The American Leather Chemists Association

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EIGHTEENTH ANNUAL MEETING

The eighteenth annual meeting of the A. L. C. A., held at the Hotel Ambassador, Atlantic City, N. J., June 9th, 10th and 11th, proved to be a very successful and well attended meeting. The meeting was called to order at 10 o'clock on the morning of June the ninth by Pres. F. H. Small and was opened by his address which was followed by the report of the Secretary-Treasurer as follows:—

SECRETARY'S REPORT

1920-1921

Total number of Active Members June 1, 1921	177
Total number of Associate Members June 1, 1921	230
Total number of Mutual Members June 1, 1921	99
Total Membership	506

TREASURER'S REPORT

May 1, 1921 to June 1, 1921.

RECEIPTS.

Cash on hand May 1, 1921		$1744.48
Dues and Subscriptions	5013.66	
From Advertisements	3704.07	
Sales—Volumes, Journals, Index	1051.98	
From Interest and Exchange	13.62	
Refund—Money not expended at Annual Meeting	100.00	
Loan on Liberty Bond	679.00	
Loan from Mr. Saxe	1000.00	
Austrian Relief Fund	275.00	
		11837.33
Total Receipts		13581.81

DISBURSEMENTS

Publication of Journal	5176.01
Reprints	1468.34
Year booklet of membership	113.84
Binding Volumes	596.29
Index	85.00
Journal expense—Insurance, copyright, etc.	144.38
Editor's expense	523.86
Secretary's expense	1572.50
For back numbers of Journal	38.65
Printing, multigraphing, etc.	315.19
Council Meeting expense	73.64
Annual Meeting expense	363.82
Dues to S. L. T. C.	7.50
Interest and bank charges	49.83
Miscellaneous expense	395.41
Paid on Loan from S. Saxe	500.00
Austrian Relief Fund disbursement	271.33
	11695.59
CASH ON HAND JUNE 1, 1921	1886.22

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The Effect of Atmospheric Humidity on the Determination of Moisture in Leather was the subject of a paper by T. D. Jarrell which was read by F. P. Veitch in the absence of the author. Mr. Veitch as chairman of the Committee on the Estimation of Oils and Greases in Leather then presented the report of the work of this Committee. The morning session closed with the report of the Committee on the Determination of the Sugar Content of Leather by J. S. Rogers, chairman.

The afternoon session was opened with a paper on the Soaking and Liming of Hides by C. M. Morrison in which the author described some modern practices in conducting beamhouse processes. G. A. Kerr followed with a paper on the Relation of South America to the Leather Industry in which the author discussed at some length and in detail the production of hides, skins and tanning materials in South America. This paper was followed by the report of the Committee on Sampling and Preparation of Leather for Analysis. Mr. Small as chairman of this Committee gave a brief review of the work which happens to be the most extensive and comprehensive work of this nature that has yet been done and concluded his report with recommendations as to where and how to sample the various cuts of leather. Some Applications of Synthetic Tanning Extracts was the subject of a paper by J. B. Hill and G. W. Merryman which evoked much interest. G. D. McLaughlin then read a paper on Some Effects of Post-Mortem Changes in Fresh Hides which is his second paper on the study of hide that he is pursuing as Director of the American Leather Research Laboratory. The afternoon session was closed with a paper by R. W. Frey on the Explosiveness of Tannery Dusts. The author was forced to forego demonstrating his paper because of the violence of the explosion and unsuitability of the convention hall for such.

Friday morning, the meeting was called to order promptly at 10 o'clock and was opened with the committee report on the Determination in Leather of Matter Extractable by Water [see this JOUR. **16**, 264 (1921)] a summary of which was given by G. W. Schultz in the absence of the chairman. After a paper entitled Notes on the Extraction of Leather with Water, by F. P.

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Veitch and R. W. Frey considerable discussion followed on this phase of leather analysis. Then followed a paper by G. W. Schultz on Further Observations on the Wilson-Kern Method of Tannin Analysis, wherein it was claimed and demonstrated that this method does not give the true tannin content of vegetable tanning materials. The morning session was closed with the report by A. A. Claflin of the Committee investigating the Claflin method of measuring the plumping power of tan liquors.

The afternoon session was opened with a paper by R. W. Griffith on Chestnut Wood Tannin, which appears in this issue of the JOURNAL. L. J. Robertson, accredited and official representative of the Tanners' Council to the meeting, presented an interesting paper on the Conditions in the Leather Industry. The extemporaneous remarks of Mr. Robertson as to the appreciation of the work and aims of the Association were certainly a great source of encouragement to the leather chemist and a great satisfaction to those who have so faithfully worked for the cause of our Association. Prof. H. N. Holmes then lectured on Colloids. The subject was so clearly and attractively presented by Prof. Holmes that one could not help but feel envious of his students who are able to have before them always in the course of their studies such a tremendous inspiration. Dr. L. Balderston then presented an interesting paper on the Tanning Materials in the Far East which was based on personal observations. This session was closed with a paper on the Determination of Available Calcium Oxide in Lime Used for Unhairing Hides by F. P. Veitch and T. D. Jarrell.

Saturday morning, the final session of the meeting was opened with a paper by R. W. Frey and I. D. Clarke on Rapid Washing of Chromed Hide Powder, which was followed by the Committee reports on the Color Measurement of Vegetable Tanning Solutions and the Determination of Epsom Salts in Leather presented by their chairmen, T. Blackadder and R. W. Frey respectively. The meeting then resolved into executive session. After a count of the ballot it was found that the proposed changes in by-laws [See this JOUR. **16**, 108 (1921)] had been adopted. There was only one opposing vote. G. D. McLaughlin and G. W. Schultz were elected as members of the Council.

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ON CERTAIN CHARACTERISTICS OF FRESH STEER HIDE.

By George D. McLaughlin.

FROM THE DEPARTMENT OF LEATHER RESEARCH, OF THE TANNERS' COUNCIL, IN THE UNIVERSITY OF CINCINNATI.

Received May 10, 1921.

The purpose of this article is to show the effect of certain acids, alkalies and salts on the swelling of fresh hide. By fresh hide is meant hide which enters the solutions to be studied within thirty minutes from the time it leaves the animal's body. We have been unable to locate any published work of this nature. Eitner[1] studied the soaking of fresh calf-skin which had been first dried at various temperatures, Von Schroeder[2] treated fresh hide with brine and then studied the liming and sweating process and Stiasny[3] studied the liming process on fresh calf-skin which was salted and the salt subsequently washed out. We used original hide without any preliminary treatment.

METHOD

Our specimens were all taken from heavy steers, of medium length of hair. We cut to a width of six inches on each side of the back-bone and eighteen inches up from the tail-root. Such hide possesses a uniform structure and water holding capacity, as our previous studies have shown.[4] This strip was clamped into a frame and the hair, epidermis, flesh and fat rapidly split off with a power-driven circular knife, avoiding any heating of the hide through friction in splitting. In short, we dealt with the corium, or "true skin"; corium constitutes the bulk of the hide content of leather. Following the splitting process the corium was passed rapidly through distilled water and cut into properly sized pieces, which were blotted with filter-paper, weighed on a sensitive balance and placed in the solution to be studied. Unless otherwise stated they remained in the solution twenty-four hours, when they

[1] *Gerber*, page 112 (1880).
[2] *Gerberei-Chemie*, page 646 (1898).
[3] *Der Gerber* (1906), reprinted in *Jour. S. L. T. C.*, **3**, 129 (1919).
[4] This JOURNAL, **15**, 228 (1920); Ibid., **15**, 557 (1920).

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were again quickly passed through distilled water, blotted and weighed. Dividing the second weight by the first gives the percentage of weight gain or loss. Twenty-five grams of corium, containing approximately sixty percent water, and two hundred and fifty cc. solutions were employed. Temperatures averaged 20° C. In choosing a twenty-four hour soaking period we are aware that complete equilibrium is obtained by certain of the organic acids only after one hundred and twenty hours, or longer. Approximate equilibrium occurs in twenty-four hours however. In the case of alkalies, practical equilibrium is established in twenty-four hours, except NaOH or KOH, when rapid digestion occurs in concentrations of N/2 or greater, after twenty-four hours. Practical equilibrium seems to become established by the mineral acids, as well as the chlorides and sulphates, in twenty-four hours.

Finally, we would point out that we were interested in accumulating experimental facts, regardless of whether our experiments may have involved the phenomena of varying solubility of corium in the several reagents employed, double decomposition of reagents, hydrolysis of salts, etc.

Experimental Findings

Corium soaked in varying concentrations of different acids showed the percentage of weight gain (swelling) outlined in Table 1 and Figures I and II. In the figures the horizontal line shows the concentration of reagent and the vertical line the percent of swelling.

Removing the corium from the various acid solutions and soaking it for a second twenty-four hours in N/20 lactic acid gave the results shown in Table 2 and Figure III, which express the total swelling at the end of the forty-eight hour period.

Turning to the alkalies, we have the results shown in Table 3 and Figure IV.

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TABLE 1

Acid	5/1000 N		1/100 N		5/100 N		10/100 N		20/100 N		50/100 N		100/100 N	
	% Gain	Parts H_2O absorbed per 1 part reagent absorbed	% Gain	Parts H_2O absorbed per 1 part reagent absorbed	% Gain	Parts H_2O absorbed per 1 part reagent absorbed	% Gain	Parts H_2O absorbed per 1 part reagent absorbed	% Gain	Parts H_2O absorbed per 1 part reagent absorbed	% Gain	Parts H_2O absorbed per 1 part reagent absorbed	% Gain	Parts H_2O absorbed per 1 part reagent absorbed
Lactic [1]	11.3	41	31.2	57	53.3	36	44.8	28	46.1	11	41.0	5	54.8	1
Acetic	3.3	23	5.9	32	21.3	29	32.0	26	33 5	17	37.7	6	37.9	4
Formic	10.4	97	20.3	85	41.6	48	45.2	39	45.7	28	38.5	8	41.3	6
Butyric	0.2	0.4	1.2	4	26 2	29	37.3	25	34.7	22	34.6	8	43.4	4
Citric	1.6	10	7.1	32	35.6	24	42.5	15	48.1	13	39.4	5	33.5	2
Oxalic	8.6	35	21.5	36	38.0	12	36.2	8	24.3	3	19.7	1	20.6	0.3
Hydrochloric	23.8	191	36.1	134	34.2	32	30 6	23	18.6	13	10.4	3	2.2	water lost
Sulphuric	9.3	44	29.7	71	29.3	17	26.4	15	25 4	11	17.0	6	10.2	2
Nitric	14.1	53	30.5	59	32.8	17	25.4	12	13.2	5	2.8	Water lost	2.5	water lost

[1] NOTE—Some of the supposedly c. p. lactic acids on the market contain impurities which prevent proper swelling and should be avoided.

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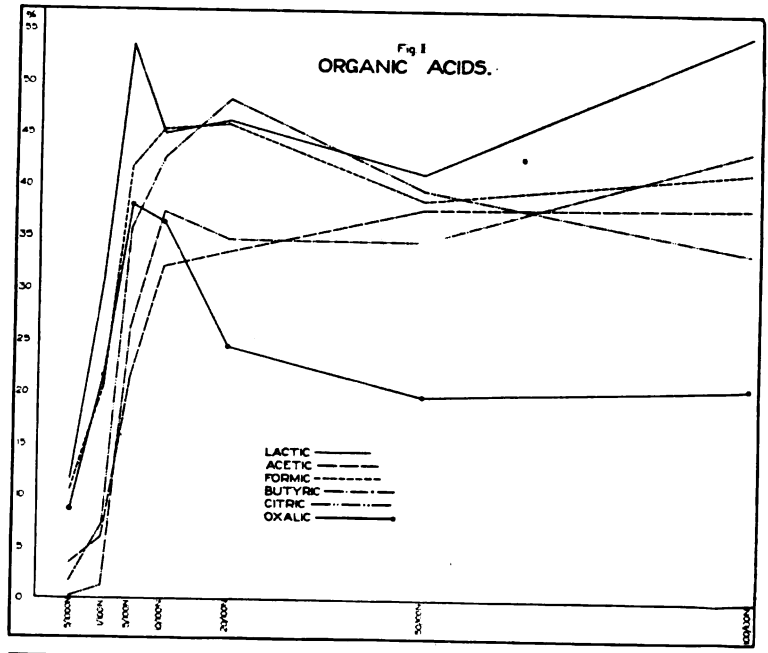

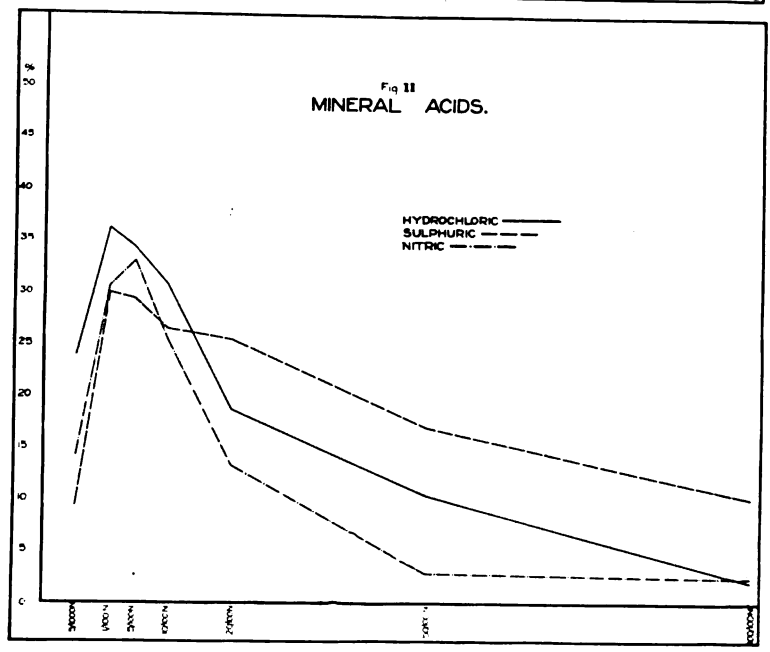

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After studying acids and alkalies we studied chlorides and sulphates. Soaking corium in different chlorides gave the results shown in Table 4 and Figure V. Removing the corium from the various chloride solutions and soaking for twenty-four hours in N/20 lactic acid gave the results shown in table 5 and Figure VI, which express the total swelling for the forty-eight hour period. Or, removing the corium from the various chlorides and soaking twenty-four hours in N/20 NaOH gave the results shown in Table 6 and Fig. VII.

Similar experiments with sulphates are shown in Tables 7, 8 and 9 and Figures VIII, IX and X.

Soaking corium for twenty-four hours in solutions of urea and pyridine gave the results shown in Table 10.

TABLE 2.—ACIDS AND N/20 LACTIC ACID

ACID	5/1000 N % Gain	1/100 N % Gain	5/100 N % Gain	10/100 N % Gain	20/100 N % Gain	50/100 N % Gain	100/100 N % Gain
Acetic	37.4	36.4	36.8	43.7	40.5	45.0	44.1
Formic	42.0	54.9	53.9	55.0	55.9	43.3	47.3
Butyric	40.9	44.0	46.5	55.9	48.6	44.3	55.0
Citric	40.3	40.5	41.8	55.7	54.0	44.8	36.0
Oxalic	38.9	36.0	45.0	42.2	30.0	28.3	30.2
Hydrochloric	46.0	46.2	35.1	34.0	28.1	22.4	14.1
Sulphuric	50.9	49.7	34.8	32.7	31.6	23.1	15.5
Nitric	46.7	51.5	41.0	39.0	25.4	21.9	16.0

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TABLE 3—ALKALIES

ALKALI	5/1000 N		1/100 N		5/100 N		10/100 N		20/100 N		50/100 N		100/100 N	
	% Gain	Parts H_2O absorbed per 1 part reagent absorbed	% Gain	Parts H_2O absorbed per 1 part reagent absorbed	% Gain	Parts H_2O absorbed per 1 part reagent absorbed	% Gain	Parts H_2O absorbed per 1 part reagent absorbed	% Gain	Parts H_2O absorbed per 1 part reagent absorbed	% Gain	Parts H_2O absorbed per 1 part reagent absorbed	% Gain	Parts H_2O absorbed per 1 part reagent absorbed
Ammonium Hydroxide	5.4	822	6.5	197	14.4	31	13.8	16	16.1	8	15.2	3	21 2	1
Potassium Hydroxide	12.9	79	17.7	49	17 9	17	17.0	13	15.3	9	19.4	4	41.9	4
Sodium Hydroxide	8.9	71	17.2	71	20.4	30	21.8	23	22 8	14	24.5	8	42.0	6
Barium Hydroxide	6.8	27	16.6	24	15.9	8	16.9	6	17.8	5				
Calcium Hydroxide	7.3	68	13.3	69	15.8	13								

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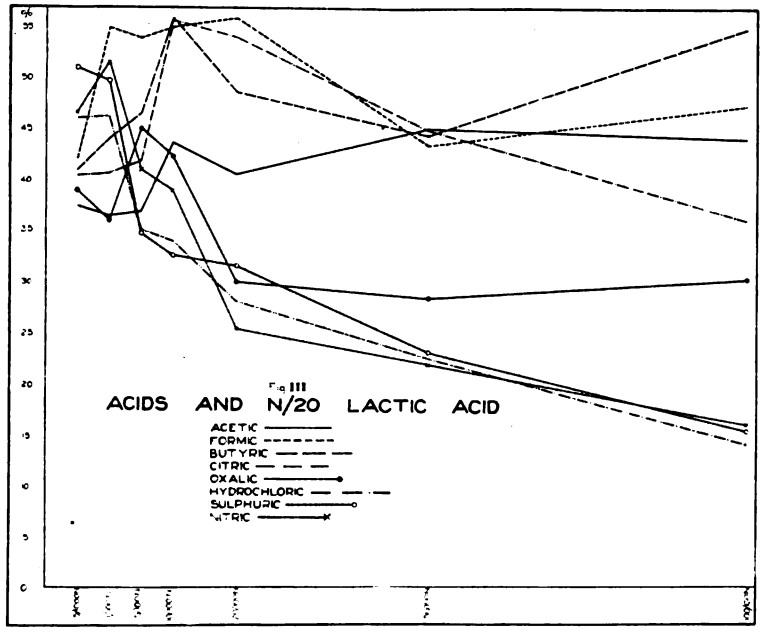

Fig III
ACIDS AND N/20 LACTIC ACID

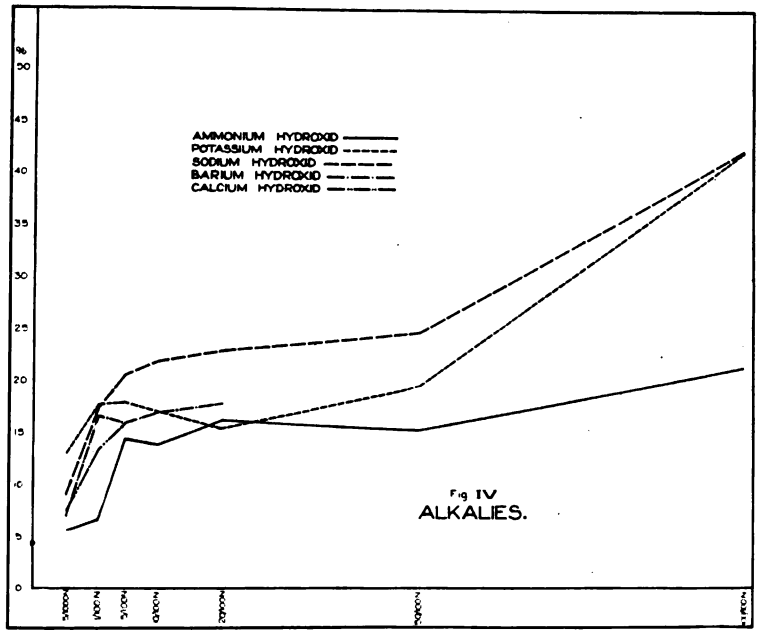

Fig IV
ALKALIES.

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TABLE 4—CHLORIDES

	5/1000 N % Gain	1/100 N % Gain	5/100 N % Gain	10/100 N % Gain	20/100 N % Gain	25/100 N % Gain	50/100N % Gain	100/100N % Gain
Ammonium chloride	3.8	0.9	5.1	6.7	10.8		10.9	9.6
Potassium chloride	2.2	1.8	4.0	6.8	9.7		10.9	9.5
Sodium chloride	1.5	2.5	3.1	7.1	8.6		10.2	9.8
Lithium chloride	3.7	3.6	5.0	4.0	5.1		5.6	5.1
Magnesium chloride	0.9	0.7	1.3	2.1	7.0		5.7	5.7
Calcium chloride	1.1	1.4	3.1	5.6	6.6		9.7	8.9
Cupric chloride	2.1	3.5	3.0	2.7	3.8		2.0	1.6
Ferric chloride	18.7	17.8	26.1	20.7	13.7		0.9	−18.9
Mercuric chloride	−0 4	0.2	−1.0	even	0.9	1.7		

TABLE 5—CHLORIDES AND THEN N/20 LACTIC ACID

	5/1000 N % Gain	1/100 N % Gain	5/100 N % Gain	10/100 N % Gain	20/100 N % Gain	25/100 N % Gain	50/100 N % Gain	100/100 N % Gain
Ammonium chloride	36.0	36.9	35 2	33.0	31.7		29.3	21.6
Potassium chloride	37.0	30.5	28.4	25.3	22.1		19.5	16.8
Sodium chloride	37.6	40.9	40.2	42.1	30.8		26.0	22.7
Lithium chloride	45.7	28.3	30.6	32.0	32.9		24.3	16.7
Magnesium chloride	35 8	37.7	32.0	31.6	24.5		19.2	16.3
Calcium chloride	46.0	40.5	41.6	30.8	35.6		31.1	18.0
Cupric chloride	32.5	32.0	33.7	34.1	35.1		36.9	35.9
Ferric chloride	43.1	33.8	34.2	34.9	32.9		27.9	21.0
Mercuric chloride	31.0	35.7	25.9	23.4	21.8	29.0		

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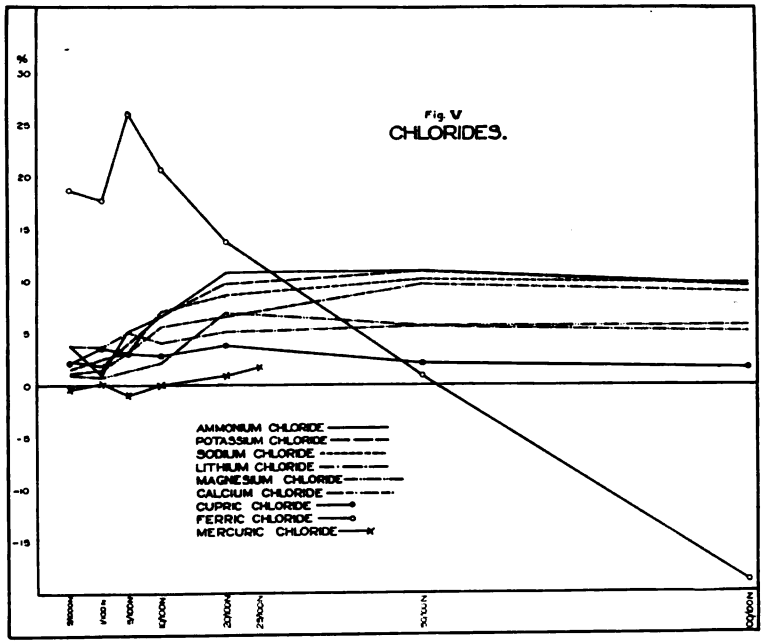

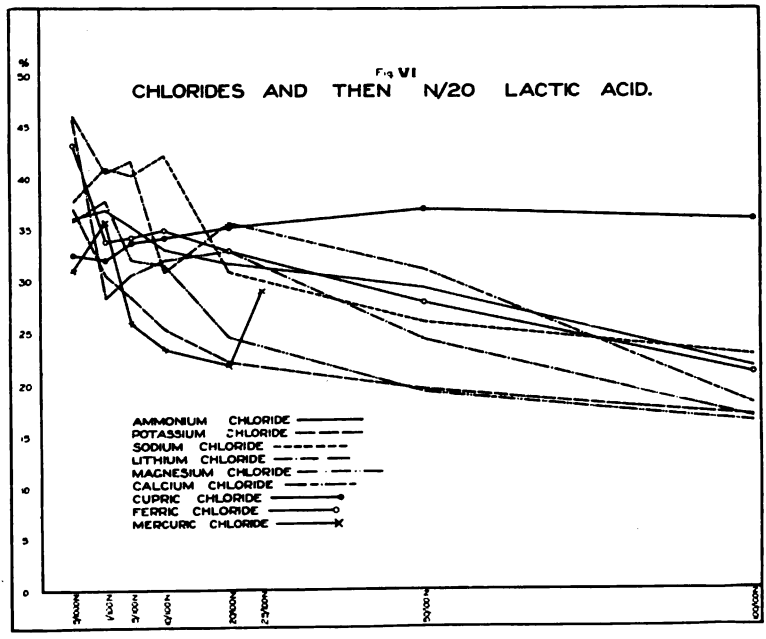

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TABLE 6.—CHLORIDES AND THEN N/20 NaOH

	5/1000 N % Gain	1/100 N % Gain	5/100 N % Gain	10/100 N % Gain	20/100 N % Gain	25/100 N % Gain	50/100 N % Gain	100/100 N % Gain
Ammonium chloride	16.5	16.8	16 9	20.0	22.3		14.9	9.9
Potassium chloride	16 6	15.3	15.6	16.9	17.3		17.9	13.7
Sodium chloride	21.5	18.3	19.6	19.0	21.6		21.2	18.8
Lithium chloride	20.8	24.2	23 0	20.5	19.3		19.6	19.8
Magnesium chloride	16.8	18.2	17.6	15.2	15.0		13.8	4.3
Calcium chloride	18.2	14.9	15.9	17.6	19.6		14.5	7.2
Cupric chloride	19.0	26.8	24.6	17.9	13.2		10.5	4.8
Ferric chloride	17.5	23.9	28.1	23.8	16.8		12.3	8.9
Mercuric chloride	15.7	15.9	8.6	6.1	3.3	3.4		

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TABLE 7—SULPHATES

	5/1000 N % Gain	1/100 N % Gain	5/100 N % Gain	10/100 N % Gain	20/100 N % Gain	50/100 N % Gain	100/100 N % Gain
Ammonium sulphate	1.7	1.1	8.8	12.0	11.4	7.3	2.8
Potassium sulphate	2.7	3.4	4.8	7.8	6.1	5.9	4.1
Sodium sulphate	1.9	2.0	2.9	3.1	6.3	6.7	3.1
Lithium sulphate	2.2	1.4	2.3	6.0	9.2	9.6	7.3
Magnesium sulphate	0.9	0.9	1.8	0.6	4.6	4.9	0.9
Cupric sulphate	−0.4	even	0.3	0.2	1.0	−2.7	−0.9
Ferric sulphate	5.5	8.2	13.5	9.5	7.8	5.9	8.5
Nickel sulphate	0.5	−0.3	even	2.4	8.4	6.5	
Zinc sulphate	1.1	even	0.3	0.4	2.3	−0.4	−6.0

TABLE 8—SULPHATES AND THEN N/20 LACTIC ACID

	5/1000 N % Gain	1/100 N % Gain	5/100 N % Gain	10/100 N % Gain	20/100 N % Gain	50/100 N % Gain	100/100 N % Gain
Ammonium sulphate	29.8	30.7	25.9	29.0	18.4	16.0	16.5
Potassium sulphate	27.3	37.9	35.8	30.2	25.3	16.7	15.9
Sodium sulphate	37.5	38.6	32.4	23.1	20.0	10.2	11.9
Lithium sulphate	27.3	35.3	29.9	34.7	20.6	18.7	11.2
Magnesium sulphate	34.6	24.7	25.8	22.4	20.3	15.2	13.1
Cupric sulphate	27.7	27.9	22.9	21.2	20.9	17.4	16.7
Ferric sulphate	29.5	28.5	18.5	11.8	10.6	8.9	12.8
Nickel sulphate	27.9	25.9	22.4	20.1	19.8	13.2	
Zinc sulphate	26.8	24.8	22.6	19.7	19.9	16.8	13.1

TABLE 9—SULPHATES AND THEN N/20 NaOH

	5/1000 N % Gain	1/100 N % Gain	5/100 N % Gain	10/100 N % Gain	20/100 N % Gain	50/100 N % Gain	100/100 N % Gain
Ammonium sulphate	28.6	17.9	18.6	18.0	12.4	8.7	3.4
Potassium sulphate	17.1	15.7	18.8	21.2	16.7	19.4	16.7
Sodium sulphate	21.6	13.4	16.3	12.7	15.9	15.0	14.1
Lithium sulphate	11.7	12.7	14.7	12.7	15.4	14.9	12.8
Magnesium sulphate	15.6	14.8	15.1	13.3	13.6	9.8	9.7
Cupric sulphate	18.3	16.0	18.9	14.5	13.1	5.9	3.7
Ferric sulphate	17.1	16.7	17.9	14.0	10.1	7.1	6.4
Nickel sulphate	11.8	15.8	10 9	12.9	13.4	7.1	
Zinc sulphate	16.9	14.2	13.5	14.4	11.7	7.6	−0.6

TABLE 10—PYRIDINE AND UREA

	5/1000 N % Gain	1/100 N % Gain	5/100 N % Gain	10/100 N % Gain	20/100 N % Gain	50/100 N % Gain	100/100 N % Gain
Pyridine	1.1	0.5	0.4	0.5	even	1.9	1.6
Urea	1.0	1.0	0.9	0.9	1.1	3.7	3.3

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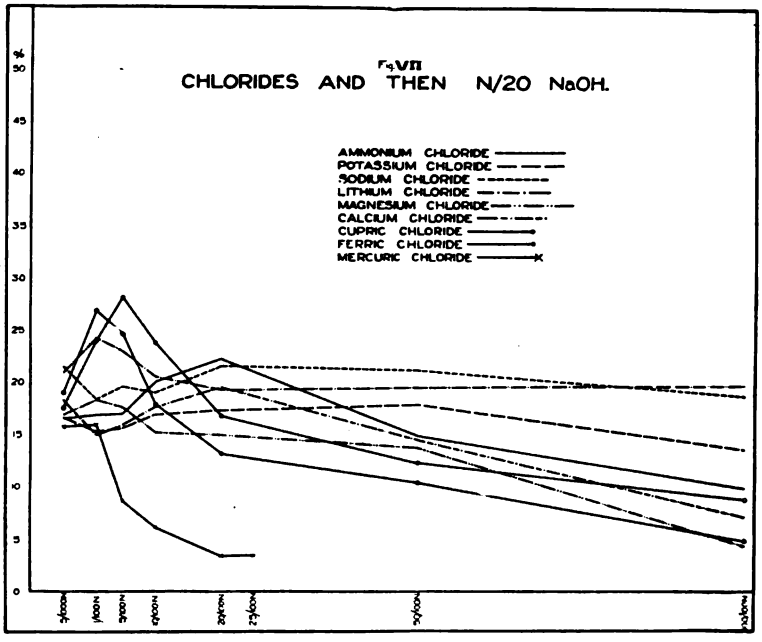

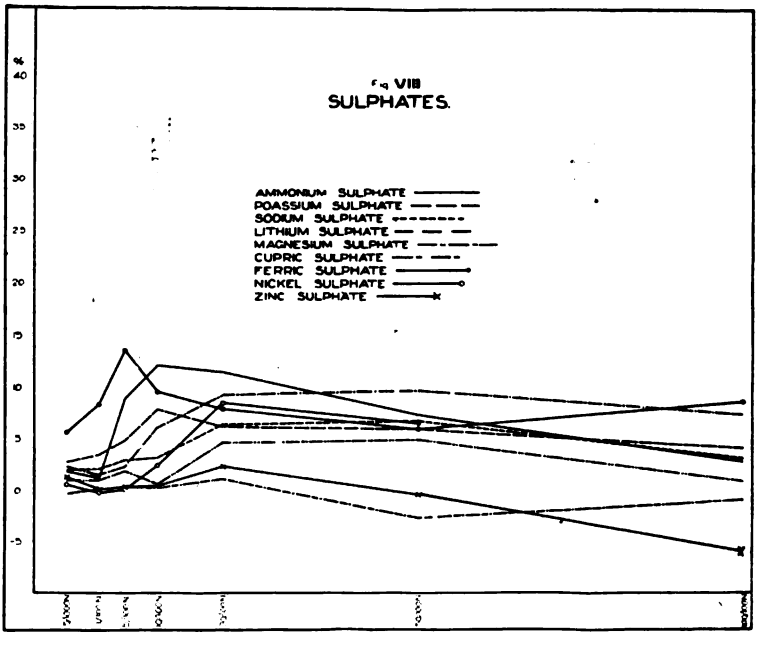

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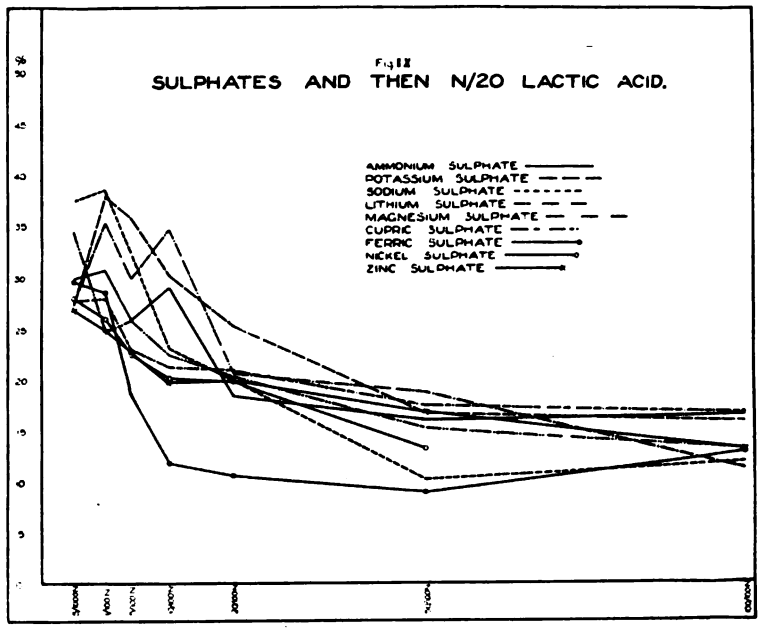

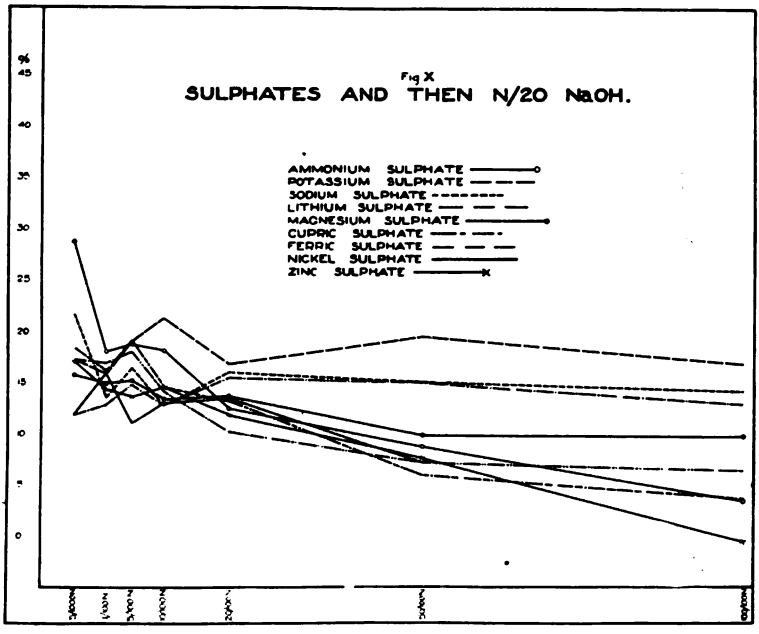

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COMMENTS

From the foregoing experimental results we note that:

(1) All of the acids employed have a swelling effect on corium, the amount of which depends upon (a) the character of the acid and (b) the concentration. In concentrations greater than 5/100 N, the organic acids show the greatest general swelling, the mineral acids the least, while oxalic acid occupies a position about midway between the two groups.

(2) When we remove the corium from the several acids and soak it further in lactic acid we observe that additional swelling occurs. The corium previously treated with the organic acids shows the greatest total swelling, the mineral acids the least, while oxalic acid again occupies the middle position. In other words, the general picture noted under (1) is repeated. It is evident that mineral acids have a special effect on corium which the organic acids do not have.

(3) All of the alkalies employed swell corium, the amount of which depends upon (a) the character of the alkali and (b) the concentration.

(4) Hides or skins are salted with sodium chloride (salt) in the packing-house; wherefore the action of various chlorides on corium is of interest. We note the effect of a chloride is dependent upon (a) its basic radical and (b) its concentration. As a general rule, the chlorides of ammonium, potassium and sodium produce the greatest swelling; lithium, magnesium and calcium occupy a middle position, while the heavy metals produce the least. The very slight swelling in cupric chloride is interesting in view of the presence of hydrochloric acid produced through hydrolysis. This illustrates the power of the copper radical. A more striking illustration of a similar phenomenon is seen with ferric chloride in which case we recognize the tremendous dehydrating power of the iron radical in the presence of hydrochloric acid. *The effect of admixture of heavy metal salts along with sodium chloride is not to be overlooked in the salting of hides or skins, nor their effect in soaks and limes.*

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(5) *From our experiments it is evident that the action of mercury bichloride is such that it must be used with due care in the disinfection of hides.* Referring to Tables 5 and 6, we note the effect of this salt on the subsequent swelling of hide by either acid or alkali, in comparison with other chlorides.

(6) While N/20 lactic acid swelled corium 53.3 percent, the subsequent total swelling was much less when the corium was first treated with chlorides. N/20 NaOH swelled the corium 20.4 percent, but we note that this figure is *increased* when we first soak the corium in certain concentrations of some chlorides.

(7) Corium treated with sulphates, as a general rule, swells less in N/20 lactic acid than corium treated with chlorides; and swells less in the subsequent bath of N/20 NaOH, with the exception of potassium sulphate.

(8) The swelling of corium in urea or pyridine is negligible whereas these reagents swell gelatin and fibrin very considerably.[5]

When fresh hide is allowed to stand for various periods before entering a saturated lime solution, its swelling capacity is materially and progressively changed. This is due to post-mortem changes in the hide; the effects of which will be the subject of our next publication.

RECENT RESEARCH IN LEATHER MANUFACTURE. *

By H. R. Procter

There is reason to fear that much of the more important research-work of recent times has been little understood by those whom it was designed to profit, and unavoidably so, since it has dealt with matters which can hardly be made clear to anyone without considerable knowledge of modern chemical theory. It is in the hope of remedying this to some small extent that I speak today, but I am very conscious that in the time at my disposal I cannot do more than give the slightest sketch of the important work which has been accomplished since I wrote the "Principles of Leather Manufacture" 17 years ago, and the most important parts of it could not be made clear without a whole course of preliminary lectures which would not interest most of my audience.

[5] Martin H. Fischer: "*Oedema and Nephritis*," 3rd Ed., **73**, 113, New York, 1921.

* Reprinted from *J. S. L. T. C.*, **4**, 282 (1920).

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I propose, therefore, to devote most of my time to the purely chemical questions, leaving the not unimportant advances in the details of practical manufacture to others. Among the practical gains, however, which are also of scientific importance, I may, however, name Dr. Stiasny's discovery of an entirely new class of artificial tanning substances: the syntans[1] which can be produced so cheaply as to have already found extensive use in the tannery. Smaller points, though not without interest, were the discovery in my laboratory that chrome tannage can be almost entirely "stripped" in the cold by solutions of salts of dibasic organic acids, such as Rochelle salt[2]; and the method of preparing "chrome extract" by direct reduction of sodium bichromate with sulphurous acid[3] which I found, after publication was already in use by one firm as a trade secret. I may also mention as a new departure, though without expressing any opinion on its commercial value, the high-vacuum tanning process of Mr. Nance. All previous attempts to introduce tan into leather by the same use of vacuum as is so successful in creasoting timber (and they were many) had failed because the pores of the hide are filled with incompressible water, instead of with air, and it was not until Nance used a vacuum so high that the water actually boiled in the pores of the hide at a temperature of only 70° or 80° Fah. that the water could be expelled, and the entry of tan-liquor made possible. A new departure in drum tannages is the use of viscous colloids, such as tragasol[4] and starch paste[5] as vehicles for the tanning extract, which allow it to be used in concentrated form, without hardening the surface or drawing the grain, and probably themselves contribute to filling the leather.

Of more scientific interest, though of less immediate commercial importance are Prof. Meunier's investigations[6] on tannage with various chemical substances, and especially with quinone, which gives one of the most perfect and resistant leathers known, though its price precludes it at present from any extended use. Quinone is a derivative of benzol; a ring of six carbon

[1] Ger. Pat. 262, 558, 1911.
[2] *J. S. C. I.* This Jour., **11**, 173, (1916).
[3] *J. R. S. A.*, **66**, 747, 776, 1918. This Jour. **14**, 30 (1919).
[4] Gum Tragasol Supply Co. Ltd., Hooton, nr. Chester.
[5] A. Turnbull and B. Carmichael, E. P., 101,470, 1917.
[6] *Coll.* **7**, 1908, p. 195. *Ibid*, **8**, 1909, pp. 58, 319. Ger. Pat. 206 957, 1909.

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atoms, dear to color-chemists, and to each carbon of which in benzol itself an atom of hydrogen is attached. In phenol (ordinary carbolic acid) the place of one of these hydrogens is taken by an OH or hydroxyl group, and the substitution of a second OH gives as might be expected, 3 di-hydroxy-phenols, alike in composition, but differing in properties, and in the place of the second OH on the ring. Taking the OH of common phenol as in the noon position, the 2 o'clock position gives catechol, the source of all the catechol tannins; the 4 o'clock is resorcin, present in the dyestuff orcin, and the 6 o'clock is hydroquinone, the common photographic developer. If hydroquinone be oxidized by exposure to the air, or otherwise, the H's of the two hydroxyls combine with the O to form water, and the spare links of the deserted O's join hands across the ring and form quinone. Such a structure is naturally little stable, and in presence of hydrogen, easily reverts to hydroquinone. In a 1 per cent solution of quinone, pelt becomes first rose-colored, then violet, and finally brown, and is converted into a soft tough leather which will stand boiling and washing with soap, or even dilute acids or alkalies, and dyes readily with acid, basic, and mordant dyes. Meunier found hydroquinone in the used liquor, thus proving that the skin had not merely combined with quinone, but with oxygen. A similar tannage can also be produced by hydroquinone, but more slowly and only in presence of air. The oxidation of the hide-substance is of some theoretical importance. Meunier concludes that the quinone combines with the amino-groups of the skin, to which apparently acids and vegetable tannins also attach themselves.

Meunier pursued his researches with other phenols and phenol derivatives, such as progallol and gallic acid, and found that most of them would tan if exposed to the oxidizing action of the air, and still more rapidly when in a slightly alkaline condition, which promotes oxidation. Gallic acid with access of air, rendered gelatine insoluble in 3 days, while gallotannic acid failed to do so in 26 days in a closed vessel, but rapidly did so when air was admitted. This seems to show that air has some function in tannage which has not been generally recognized, though whether the skin or the tannin, or both, must be oxidized is not yet clear. It may, however, be pointed out that if tannin will not tan gelatine in vacuo, it will certainly tan skin, and the reason may possibly be

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that while the tannin permeates the hide and penetrates the extremely fine fibres, it is not able to penetrate gelatine in the mass, but only tans the surface, while the insolubilization of the interior is due to the oxidation of the gallic acid which is always present in commercial tannin or is formed by its decomposition. In experiments on the diffusion of tannins in gelatine jelly, I have found that this is apparently the case. Meunier's statement that gallic acid tans more rapidly in alkaline solution is noteworthy, and shows that its mode of action is radically different from that of the tannins, which will only tan in an acid medium. The work throws an important and rather unexpected sidelight on the vexed question of the value of the phenolic non-tans, such as gallic acid which are present in all tanning materials. Though partially absorbed by hide powder in the ordinary analytical process, they certainly do not tan, and Wilson[7] has shown that they can be removed from it by washing, but it is clear that if exposed to the air in drying, they will become fixed by oxidation, producing an actual tanning, and adding to the weight and solidity of the leather. These facts will have to be considered in any revision of the analytical method. The ideal analytical method of the future should give much more detailed information as to the constituents of the tan, but will consequently cost more in execution, for which users will have to pay, and the present process, imperfect as it avowedly is, has become of such commercial importance that no changes, even for the better, can be lightly undertaken.

Meunier[8], following up the clue of oxidation, next experimented with such well-known oxidizing agents as chlorine, bromine and iodine, all of which precipitated gelatine from its solutions as insoluble compounds, and found that all were capable of converting skin into leather. Bromine, especially, in dilute solution, and with addition of salt to prevent undue swelling from the hydrobromic acid produced, speedily tanned the skin, which after washing with water, and more rapidly with a solution of sodium bisulphite to remove the surplus bromine, formed a white, supple and fine-grained leather of considerable toughness and resistance even to hot water, and which contained about 0.9 per cent. of

[7] This JOUR., **15**, 295 (1920).
[8] Le tannage au brome. *Coll.*, **10**, 1911, pp. 289, 373.

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bromine on the dry gelatine. Equally good, and very similar results were obtained by the use of sodium hypobromite, formed by adding soda to the bromine solution till its yellow color was just discharged, and in this case salt was not necessary, though the washing with water and bisulphite could not be omitted.

As bromine is too expensive for ordinary use, it seemed desirable to experiment with the much cheaper chlorine, but gaseous chlorine or chlorine-water broke up and dissolved the gelatine before rendering it insoluble. Much better results were obtained with sodium hypochlorite (*eau de javelle*) and with bleaching powder, but more care was required than with bromine, and it was necessary to work at temperatures at or below 10° C. (50° Fah.) which would be difficult in practice in summer, but Meunier suggests the use of the process for the temporary preservation of skins in place of pickling, or for their preparation for other tannages, and this might be practicable where very cold well-water was available. Ordinary "hypo" might no doubt be substituted for bisulphite for washing out the excess of hypochlorite.

In all these cases the tannage appears to be wholly chemical, and no solid body which could coat the fibres is produced, so that neither Knapp's theory of coating the fibres, nor the more modern ideas of adsorption can well apply. They give some color, however, to a theory of Fahrion's which will be mentioned later as to the necessity of oxidation of the fibre itself.

To complete his investigations as to the theory of tannage, Meunier next experimented with a purely physical tannage by dehydration and isolation of the fibres on the principle of Knapp's alcohol leather[9], but instead of alcohol, he employed solutions of potassium carbonate, which have a very high osmotic pressure and affinity for water. Placed in strong solutions, up to 80 per cent. water flowed freely from the skin under the osmotic pressure of the solution, which seemed scarcely to penetrate it, and in a few hours left it in a state when after "putting out" with the sleeker, or even wiping with a cloth, it could be dried rapidly in the air, and after staking formed a soft white leather which was permanent so long as dry, but returned rapidly to pelt when soak-

[9] *Coll.*, **11**, 1912, pp. 54, 420.

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ed in water. As very little potassium carbonate is actually absorbed, there is a commercial possibility of using this process as a substitute for pickling.

Another interesting set of experiments were made by repeating similar experiments in duplicate with potassium carbonate, and adding to one set 3 cc. per litre of commercial formaldehyde solution. Where the potassium carbonate solutions were of less than 10 per cent., the leather of both series dried hard and horny, and more concentrated ones were necessary for good results. In each series the skin was equally leathered, but while those with the carbonate alone returned to pelt on soaking, those with formaldehyde, when re-dried were as soft as before. Meunier concludes from this that the function of the sodium carbonate in the Payne & Pullman process is merely that of dehydration, and not as an alkali. I am not myself quite convinced on this point, since their patent specifies only 1.9 to 2.8 per cent. of sodium carbonate which is less dehydrating than the potassium salt, and in Meunier's experiments would be quite insufficient to produce a soft leather, while I can say from my own observation that Pullman's skins were perfectly leathered in the drum. It is, however, certain that satisfactory formaldehyde leather can be produced in the presence of other salts which are not alkaline. Meunier's opinion of formaldehyde as a tanning agent is not a very high one. He states that it slowly evaporates on exposure to air, leaving the leather hard and brittle, and that it can be removed by continued treatment with hot water, being in that respect very inferior to his quinone tannage. We have found at Leeds that formaldehyde can be quantitatively recovered from leather by hydrochloric acid so weak as decinormal.

In connection with what has been said on new tannages, it is perhaps worth while to mention the accidental discovery of one in which I had a part. I had noticed in the laboratory the powerful dehydrating effect of saturated solutions of ammonium sulphate, which easily produce a white leather like Meunier's, and I communicated this to Mr. Seymour-Jones, thinking it might be useful in some cases where the use of acid in pickling is objectionable. He tried it on a practical scale, but using commercial ammonium sulphate, which contains traces of tarry phenolic prod-

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ucts, and found to his disappointment that the leather was permanent, and would not return to pelt. It is quite possible that by the choice of suitable tar-products, a leather might be made of commercial value.

Leaving Prof. Meunier, I must turn to the work of some other chemists. It was noticed by Lüppo-Cramer[10] that colloidal silver peroxide precipitated in the gelatine film of photographic plates, rendered it insoluble in hot water, and that it had the same effect on gum-arabic and starch. More recently, Dr. Erich A. Sommerhoff discovered that colloidal precipitates, such as hydroxides, sulphides, phosphates and silicates of the heavy metals, when drummed into pelt, rapidly produced complete tannage, and, what is much more surprising, that ultramarine, a fine and quite insoluble powder, had a rapid tanning effect. It has long been known that leather could be formed by the precipitation of such bodies in or on the fibre:—Phosphate leathers have been commercially produced, and the "pyrotan" process owes at least part of its efficacy to a similar effect. Leathers have also been made, not only by chrome and alumina, but by other metals producing basic salts hydrolyzed by the skin; and it has long been known that two-bath chrome leather owes its superior softness to that of basic tannage to the sulphur deposited on the fibre.

Instances of this sort might be multiplied almost *ad infinitum*, but enough has been said to show that no single theory of tannage can embrace all possible cases, and that in most commercial processes, more than one of these actions is involved.

Perhaps I may be excused if I deal now with another fundamental advance in tanning theory[11] in which I have myself taken a large part, though many of its later developments are due to my

[10] *Coll.*, **7**, 1908, p. 24.

[11] "Action of acids and salt-solutions on gelatine," H. R. PROCTER. This JOUR., **6**, 270, 1911.
"Equilibrium of dilute hydrochloric acid and gelatine," H. R. PROCTER. *J. Chem. Soc.*, **105**, 1914, 313. This JOUR., **9**, 207, (1914).
"Acid-gelatine equilibrium," PROCTOR & WILSON. *J. Chem. Soc.*, **109**, 1916, 307. This JOUR., **11**, 261, (1916).
"The swelling of colloid jellies." PROCTER & WILSON. This JOUR., **11**, 339, 1916.
"Colloidal phenomena and the adsorption formula," J. A. & W. H. WILSON. *J. Am. Chem. Soc.*, **40**, 1918, 886.
And other papers.

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collaborators, and especially to Mr. J. A. Wilson:—I mean the swelling of gelatine and hide under the influence of weak acid and alkaline solutions. To explain it fully to those who have had no training in modern chemistry would involve a preliminary discussion of the theories of ionization and osmotic pressure for which there is no time, and I must therefore address myself mainly to those of my audience who already have some knowledge of the subject.

In what I am now about to say, I must ask you to strain your power of scientific imagination to the utmost limit; that power by which you see in the eye of the mind things which can never be seen by the bodily eye, but which is the only guide in the higher walks of scientific research.

We know that the small particles of all bodies are in a state of rapid vibratory motion which we call *heat*. This is the cause of the expansion and pressure of gases, which perpetually bombard and push the walls of the vessels which contain them. It is rendered visible to the eye by the constant tremor of small particles like bacteria under the higher powers of the microscope, which are pushed about this way and that by the impact of the molecules. When substances are dissolved in liquids, their particles, loosened from each other, behave in the same way as those of a gas. They cannot, of course, escape from the liquid, but tend to spread themselves through the whole of it, and if some obstacle is interposed through which the liquid can pass, but the molecules of the dissolved body cannot, they push upon the obstacle and exert what is called *osmotic* pressure. If a bladder be half-filled with strong spirit (preferably not modern whiskey, but methylated spirit will do), tied up and put into water, the spirit particles which cannot get through the bladder will push out its walls, the water will slowly pass in to fill the vacant space and the bladder will swell till it is full. If a lump of gelatine jelly, or a piece of wet hide be put in strong spirit, the converse will take place, the spirit will squeeze the water out and the gelatine will become horny and almost dry. This is the principle of Knapp's alcohol leather and of Meunier's dehydration tannages.

All soluble crystalline bodies behave in this way, but while sugar produces an osmotic pressure precisely equal to that it would have if it could be converted into a gas in the same space,

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salt shows nearly double as much, and it can be shown by its electrical conduction that it contains nearly double the number of pushing particles. We can only account for this by supposing that the solution of salt does not stop at the mere distribution of NaCl molecules in water, but goes on to a sort of super-solution in which the Na and Cl are separated from each other, and each pushes on its own account. The recognition of this fact is perhaps the greatest achievement of modern chemistry, and explains clearly all sorts of facts which 40 years since were insoluble puzzles. This super-solution is called "ionization" and the free elementary atoms are "ions," differing from the molecular elements as we know them in each having the equal + or — electrical charges which held them together in the molecule, and the attraction of which constitutes chemical affinity. The ions cannot pass out of the liquid in which they are dissolved, and no doubt satisfy their chemical affinities by attaching themselves to the atoms or molecules of the solvent. Only some liquids will ionize and water is probably the most powerful ionizing solvent known.

Salts usually ionize very freely, but also acids and alkalies which may be regarded as salts of hydrogen H^+, or of hydroxyl OH^- respectively; the acids into H^+ and an acid-forming group, and the alkalies into OH^- and a base: and it is on the concentration of H^+ and OH^- respectively that the qualities of acidity and alkalinity depend, and the "strength" of the acid or alkali is due; "strong" acids and alkalies such as hydrochloric acid and caustic soda being almost wholly ionized even in pretty strong solution, while "weak" ones like acetic acid and ammonia require immense volumes of water for an equal ionization.

Since the swelling power of acids for hides, and most of their other effects in tanning, depend not on their normality but on their concentration in actual ionized hydrogen, it is clear that we want some other measure of "strength" than titration. Let us be quite clear on this point. To neutralize a certain quantity of lime, we need an equal quantity of normal acid, whatever the acid is, and in this respect titration is a correct measure of acid concentration, but as regards swelling there is all the difference in the world between hydrochloric and acetic. What we want is the actual concentration at the moment, and without dilution or concentration, of the hydrogen ion. Water itself ionizes an

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equal and very minute quantity of both hydrogen and hydroxyl ions, and the point of true neutrality of a solution is when these are equal, as in water. Since these two ions always exist in any solution in inverse quantities, the statement of either includes that of the other, and as the hydrion is the most easy to determine, it has becomecustomary to state this only. Generally this is now done in terms of the inverse logarithm of the normality of actual ionized acid for reasons which I cannot go into now, as I am not teaching a class of elementary mathematics, but some of which will become apparent as I proceed. It may, however, make the matter a little clearer if I mention that the whole numbers of the logarithmic statement correspond to the number of ciphers following the 1 in the divisor of ordinary normality: thus $P_{H^+}=2$ is 100th normal of real acidity; $P_{H^+}=4$ 10,000th normal and so on.

Anyone who has used methyl-orange and phenolphthalein as indicators in ordinary titration must have noticed that with "strong" acids and alkalies the color-change is almost simultaneous: the alkaline red of the phenolphthalein fades out and another drop of acid brings out the red of the methyl-orange, and either may be taken as the point of neutrality. If, however, the acid or the alkali is a "weak" one, a good many drops may be required to affect the change. On the logarithmic statement, methyl-orange changes about $P_{H^+}=4$ or N/10,000 and phenolphthalein about $P_{H^+}=9$, one thousand millionth normal acid, or N/100,000 alkaline (14—9), and yet in this almost vanishing region occur some of the most important changes in leather manufacture. For instance, at $P_{H^+}=4.6$ gelatine has its minimum swelling, and its "isoelectric" point where it changes from a weak base to a weak acid; acid above $P_{H^+}=4.6$ will not swell hide. An indicator changing color just at this point would be very convenient for tanners, and Mr. G. E. Knowles has pointed out that this is very approximately the case with alizarin red (the sodium salt of an alizarinmonosulphonic acid). Liquors in which it is red will not swell, those in which it is yellow will.

There are two known ways of measuring these minute acidities. The electrometric is the exact and standard one, but involves expensive and complicated apparatus, and a degree of skill and delicate handling which is not within the compass of every chemist. The other, by the change of color of indicators, is less

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exact, but sufficiently so for technical use and easy and rapid enough for everyday use. A series of indicators can be chosen which will cover the range of P_H^+ over which we wish to work, and it is only necessary to exactly match the color obtained in the liquors by those in a set of standards which are easily prepared. The difficulty of the color of the liquor itself is got over by placing a tube of the original liquor in front of the standard. This arrangement was invented by the biological chemists, aud in its simplest form only costs a few shillings. It is in regular use in at least one large tannery in this country, while in U. S. A. several have very complete electrometric outfits.

The power of fixing tannins as well as acids exists only on the acid side of the isoelectric point, but if the liquor is too acid, the acid takes the place of the tannin, and slows the process by preventing its fixation. The exact degree of acidity which is best is therefore a delicate point, and my old friend Kathreiner, whose eminence as a leather chemist none will deny, once told me that he considered it the most important of all. It is obvious, however, that it is useless to attempt to determine it by ordinary titration, which not only is not nearly sufficiently delicate, but measures quite a different thing. We all know that a litre of normal acid will neutralize the same quantity of lime, whether it be hydrochloric or acetic, but their active immediate activities are very different, the hydrochloric being nearly normal also in *hydrion* concentration, while the normal acetic acid in this respect in less than N/250. From the point of titration the acids are equal, but for sour taste and swelling power they are very different, since acetic is a "weak" acid. Let us try to be clear about this, for it is very important. It will be best explained by an analogy. Lime and caustic soda are both strong alkalies, yet one can put a barrowful of lime into a limepit without risk, while the same quantity of caustic soda would dissolve the hides. We all know the reason: the greater part of the lime does not dissolve, but remains at the bottom of the pit till it is needed to strengthen the liquor as it is exhausted by the hides. Similarly if we add to a pit equal quantities of hydrochloric and acetic acids, both apparently dissolve at once, but really the hydrochloric goes into the state of super-solution which we have called ionization, while the acetic mostly remains inactive as

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merely dissolved acid, and only ionizes gradually to a very weak solution as that which is already ionized is used up, at which strength, however, it maintains itself automatically. Thus for most purposes the "weak" acids are much safer and more suitable for tannery use than the "strong" ones, though, unfortunately, they are mostly more expensive. They have a further advantage that the ionization can be lowered to any desired extent by the addition of their neutral salts. Their swelling power for hide is also affected by neutral salts present in the liquors, so that the true acidity alone is not a complete guide to the swelling power, though it is the most important factor.

I leave recent advantages in our knowledge of bacteria and enzymes to Mr. Wood, who has done so much to clear up our knowledge of liming and wet-work, but one of the recent steps has been almost sensational and seems to have cleared up the real object of puering.

Perhaps I may conclude this address by summing up in as few words as possible what I think is our present knowledge of the theory of the vegetable tanning process itself. The tannins are probably some of them in actual molecular solution and able to penetrate the hide fibre and combine with it chemically, but most of them are what is called colloidal, suspended in the liquor in fine particles or very large molecules which have little power of diffusion or of chemical combination. It can be shown that these colloid particles have electrical charges like the ions, negative in the case of tannins, and it will be remembered that the hide in acid solution is positively charged. The two have therefore a mutual chemical or electrical attraction, and when they meet they combine. In alkaline solution, when the hide is negatively charged, this cannot take place, and tanning does not occur. This, I think, is the principal action in the early stages of tanning, but later on, when the electric charge of the hide is nearly saturated, fixation still takes place, adding to the weight and solidity of the leather. This may be due to the vague effect called adsorption, or to some residue of electrical attraction, but it affects most easily those bodies such as difficultly soluble tans, phlobaphenes and the like which have little attraction for the water and are easily precipitated; hence the importance of these bodies in giving weight. From

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Meunier's work it is evident that a further fixation occurs during the drying. Not only further insoluble products are formed by the oxidation of the excess of tannins in the hide, but by that of the non-tans, such as gallic acid and catechin, and on "ageing" the solubles no doubt still further become fixed.

ACTION OF SODIUM CARBONATE ON CHROME ALUM. *

By Louis Meunier

In the recent work of Burton (*J. S. L. T. C.*, 1920, 205) on the tanning properties of violet and green solutions of chrome some results are given to show that the green solutions of chrome alum are precipitated sooner by sodium carbonate than are the corresponding violet solutions. Since these observations touch upon an extensive work by the author on the action of sodium carbonate on chrome alum solutions, it is considered advisable to give now some results that have been obtained.

Hydrolysis of Chrome salts.—1. *Direct unstable hydrolysis of freshly prepared solutions of chromium salts*: Kruger, Siewert and Van Claeff have shown that normal chrome salt dissolved in cold water partially hydrolyzes immediately liberating a part of the acid and forming a basic salt. The extent of this direct hydrolysis depends upon the concentration and temperature. For a given dilution and temperature the equilibrium of the hydrolysis for the same chrome salt is always the same. The hydrolysis is increased as the solution is diluted and the temperature raised. Recoura has shown that a solution of normal violet chromium sulphate prepared in the cold and brought to boiling becomes green and is hydrolyzed more than the cold solution. For the concentration which he used he concluded that 1/6 of the sulphuric acid of the salt is liberated with the formation of a green basic sulphate in which 4/5 of the sulphuric acid is united with the chromium according to the formula $[Cr_4(OH)_2(SO_4)_4]\ SO_4$. The equation for hydrolysis at 100° C. is represented by $2Cr_2\ (SO_4)_3 + 2H_2O = [Cr_4(OH)_2(SO_4)_4]SO_4 + H_2SO_4$. Denham in studying the equation of Decoura concluded that the equilibrium thereby represented applied for dilutions up to about 1 mol. in 40 liters. With greater dilutions digression from this equation may equal 70%, due to the formation of more basic salts. Denham

* Translated and reprinted from *Le Cuir*, **10**, 84, (1921).

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also studied the direct hydrolysis of chromium sulphate at ordinary temperatures and confirmed the phenomenon that the hydrolysis was increased with dilution from which he proposed that at ultimate dilution the hydrolysis would be complete, giving $Cr_2(SO_4)_3+6H_2O=Cr_2(OH)_6+3H_2SO_4$. This is in accord with the dialysis experiments of Graham. If a solution of violet chromium sulphate is subjected to prolonged dialysis there is obtained a colloidal oxide of chromium containing but a trace of sulphuric acid.

2. *Reversibility of the direct hydrolysis by lowering the temperature*: Recoura has shown that upon cooling a boiling solution of chromium sulphate to ordinary temperature the hydrolysis manifest at the high temperature is slowly decreased, there being a recombination of a part of the chromium oxide with a part of the liberated sulphuric acid and the solution returns to the violet form.

3. *Changes in hydrolysis at constant temperature*: It has been noted previously that the hydrolysis of a chromium sulphate solution immediately after preparation is not definite. If the solution is maintained at a constant temperature, the degree of hydrolysis changes with the time. At 0° the change is practically nothing. Senechal in his "Physical-chemical Study of Chrome Salts" gives the changes at 31° C. for a solution of chromium sulphate of a concentration equal to 0.0023 gram molecules per liter. The electrical conductivity of the freshly prepared solution is 411.7, this decreases in 15 hrs. to a minimum of 388 and then slowly increases during several weeks. This observation shows that the changes with time involve two simultaneous influences: the one predominating at first being a polymerization of the basic salt decreasing the number of ions while the other is the effect of hydrolysis which predominates later giving an increase of ions.

Action of Sodium Carbonate on Solutions of Chrome Alum: For these experiments potassium chrome alum was chosen, and in studying the changes of its solutions the volume of sodium carbonate necessary in each case for the beginning of a permanent precipitate was determined. While this method of course does not permit following the changes with the same precision as does conductivity determinations, yet it has the advantage of sim-

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plicity and furthermore is of a practical nature in indicating the readiness with which the solutions would give up their chromium oxide if used in tanning. The first appearance of a permanent precipitate is sufficiently delicate, although to eliminate the personal equation the same operator should carry out the series of experiments. It is best to work in day light. The sodium carbonate should be added from a Mohr's burette with the delivery regulated so as to be practically constant in all experiments. The agitation of the solutions during titration should also be the same. All these factors influence the results so that the procedure should be carefully standardized. It is possible even that the nature of the glass in which the solutions are kept to study the changes over a long period has an influence, a point which it is intended to investigate. The interesting observations of Marcel Bader on the different shades obtained by acid dyes upon wool depending upon whether ordinary glass or quartz was used, show the possible influence of this factor.

1. *Action of sodium carbonate on recently prepared solutions*: Chrome alum solutions of 0.5%, 1.0%, 2.5% and 5% were prepared at 0° C. and 50 cc. aliquots of each concentration after heating for 5 mins. at certain temperatures between 0° and 100° were titrated at the given temperatures with 1% sodium carbonate solution up to the beginning of precipitation. The results are given in the following table:—

0.5% Solution prepared at 0° C.		1.0% Solution prepared at 0° C.		2.5% Solution prepared at 0° C.		5.0% Solution prepared at 0° C.	
50 cc. heat'd 5 mins. at	Cc. Sodium Carbonate	50 cc. heat'd 5 mins. at	Cc Sodium Carbonate	50 cc. heat'd 5 mins. at	Cc. Sodium Carbonate	50 cc. heat'd 5 mins. at	Cc. Sodium Carbonate
0	5.6	0	10.4	0	25.6	0	52.4
15	5.0	14	9.9	17	23.7	15	50.0
45	3.5	32	9.3	30	22.1	32	47.6
72	2.0	49	7.6	49	18.7	60	37.8
100	0.4	66	5.3	73	14.4	100	28.0
		100	1.7	100	9.4		

It must be remembered that these figures were obtained by titrating at the temperature to which the solution was heated in each case and it is evident that the figures would be decidedly different if, after heating to the various temperatures indicated, the

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solutions in each case had been cooled to 0° C. before titrating. Under the last condition there would be a decrease in hydrolysis but an increase in the quantity of sodium carbonate necessary for the appearance of a precipitate. It is concluded from the above table: (1) that at 0° C. the quantity of sodium carbonate necessary for the beginning of precipitation is practically proportional to the concentration; (2) that to the contrary at 100° C. the quantity of sodium carbonate increases much greater than the concentration; (3) that for the same concentration the quantity of sodium carbonate required for the appearance of a precipitate decreases rapidly with rise in temperature. The last would seem to be an anomoly since the hydrolysis is much greater at 100° than 0° This however is easily explained. Upon adding sodium carbonate at 0° the first portions neutralize the sulphuric acid liberated by the hydrolysis of the chrome salt but the carbonic acid thereby set free remains dissolved in the solution because of the low temperature and consequently increases the acidity which retards precipitation. At 100° on the contrary the carbonic acid is eliminated as fast as it is set free. Also at 0° there is but slight hydrolysis and the weakly basic chrome salt formed has little tendency to polymerize and consequently to precipitate. At 100° a strongly basic chrome salt is formed, which polymerizes more, its solubility decreasing with the polymerization and its tendency to precipitate thereby increasing. If at the two temperatures, 0° and 100°, sodium carbonate in excess of that required for the appearance of a permanent precipitate is added, the two precipitates are entirely unlike in composition. After thoroughly washing the precipitates in hot water, it will be found that the one formed at 0° from the violet solution is chromium hydroxide, while the one from the green solution at 100° is a basic sulphate of chromium. Upon heating 50 cc. of the 5% chrome alum solution for 5 mins. at 100° and then completely precipitating at this temperature with sodium carbonate, the precipitate formed after being thoroughly washed in hot water and dissolved in hydrochloric acid, gave with barium chloride 0.265 gms. of barium sulphate.

2. *Action of sodium carbonate upon old chrome alum solutions at constant temperature*: The quantity of sodium carbonate required for the appearance of a permanent precipitate in a

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chrome alum solution maintained at constant temperature, decreases with increase in time, the change being more rapid and greater at higher temperatures. At 0° the change is practically nothing, at 100° it is almost instantaneous. The following results were obtained upon 50 cc. portions of a 0.5% chrome alum solution using a 1% solution of sodium carbonate. The temperature varied from 15° to 18°.

Time in Days	Cc. of Sodium Carbonate.
0	5.5
1	5.0
2	4.9
3	4.8
6	4.8
8	4.6
14	4.2
20	3.7
29	2.8
45	1.9

3. *Action of sodium carbonate upon chrome alum solutions heated at constant temperature for varying periods. Reversibility of the change*: The changes of chrome alum solutions at constant temperature, measured by the sodium carbonate, are reversible upon lowering the temperature. For the same concentration the decrease is less as the period of heating is increased. The figures given here were obtained upon 50 cc. aliquots of a 5% chrome alum solution heated in closed vessels for increasing periods of time. The titrations were made at 100° and then at 15° after cooling for ½ hr.

Period of Heating.	Cc. of Sodium Carbonate	
	at 100°	After ½ hr. Cooling.
1 min.	29.0	42.5
24 hrs.	29.0	36.0
48 hrs.	29.0	32.0
72 hrs.	29.0	29.0
96 hrs.	29.0	29.0

Thus the chrome alum solution appears to become stable if the heating has been sufficiently prolonged. At 100° equilibrium is quickly obtained but it is reversible. It becomes fixed only after the solution has been maintained for several days in a closed vessel at 100° or better at higher temperatures.

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4. *Action of sodium carbonate upon chrome alum solutions with violent agitation during addition*: The quantity of sodium carbonate required for the appearance of a permanent precipitate is noticeably decreased by violent agitation. Fifty cc. of a freshly prepared 5% chrome alum solution at 15° required with hand stirring 50.5 cc. of sodium carbonate, while with a mechanical stirrer giving 300 turns per min. only 30 cc. were required. This difference is probably due to: (a) driving out of the carbonic acid by the agitation; (b) effect produced by the concentration of the basic chrome sulphate in the upper layers; (c) a slight elevation of the temperature as a result of the agitation; (d) coagulation of the polymerized basic chrome sulphate molecules. Upon considering that the addition of the first portions of sodium carbonate leads to a colloidal solution of chromium hydroxide peptized by the normal sulphate remaining, it is not surprising that agitation favors the precipitation. A similar phenomenon is observed in submitting to violent agitation a solution of chromium hydroxide peptized by soda. It is a general rule applied to many colloidal solutions and to disperse systems of the nature of emulsions and suspensions. One can from these observations foresee the role that agitation might play in its application to one bath chrome tannage.

Conclusions: From this first series of experiments it can be provisionally concluded that: (1) the quantity of sodium carbonate required for the appearance of a percipitate in freshly prepared chrome alum solutions decreases as the solution is diluted and as the temperature is raised; (2) the quantity of sodium carbonate required depends upon the age of the chrome alum solution being less as the solution ages, and leads for each temperature and each concentration to a low limit; (3) the changes of a chrome alum solution heated for a short time at constant temperature are reversible, upon cooling, whereas if the period of heating is prolonged the equilibrium tends to become fixed, especially if the heating was done in a closed vessel at 100° or more; (4) the quantity of sodium carbonate is decidedly decreased by violent agitation during addition of the carbonate; (5) in solutions of chrome alum heated to 100° and generally in very old solutions sodium carbonate precipitates a basic chrome sulphate while in cold and practically fresh solutions it precipitates chromium hy-

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droxide; (6) the action of sodium carbonate is easily explained upon considering the facts that: (a) solutions of chrome alum not only undergo hydrolysis but also that the basic chrome salts polymerize with increase in time and temperature, (b) neutralization of the sulphuric acid by the sodium carbonate is accompanied by setting free carbonic acid which is more or less eliminated by temperature and agitation. Moreover the ionization of this acid depends upon the solution in which it is freed; (c) the appearance of a precipitate results from the action of sodium carbonate both as a neutralizing agent and as a coagulating agent of the colloidal solution of chromium hydroxide or of the polymerized chrome salts.

R. W. F.

CHESTNUT WOOD TANNIN.

By Robert W. Griffith

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Tannin is a generic term which refers to a group of substances of vegetable origin which have the common property of rendering gelatine insoluble and transforming hide substance into leather. Tannin occurs very generally throughout the vegetable kingdom—in roots, wood, bark, leaves and fruit. Its function in plant physiology has never been clearly understood—whether it is a plant food, or a product of plant digestion, or an intermediate product contributing to the growth of the plant structure, or merely present as one of nature's weapons to protect the plant from the attacks of predatory insects and also of the lower forms of vegetable life, such as fungi.

The tannins of commerce are derived from every source of vegetable life. Canaigre tannin is obtained from roots, oak, hemlock and wattle tannins from barks, chestnut and quebracho tannins from wood, sumac tannins from leaves. Myrobalans, valonea and divi-divi tannins are obtained from the fruits of the respective trees. While all of these materials possess the property of converting hide into leather, they yield leathers of totally different character. Tannin generally occurs

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with the presence of glucose, starch or resin and this fact suggests an intimate relation between all these substances, but whether the latter are formed in the synthesis of the tannin, or are decomposition products of it has never been definitely established.

There are various classifications of the tannins, but the one most generally accepted is that suggested by Procter, who classifies them into two groups called pyrogallol and pyrocatechol tannins respectively. Chestnut wood tannin belongs to the pyrogallol class, whose chief characteristic is the formation of insoluble ellagic acid or "bloom".

The tanning properties of chestnut wood are not contained in a single chemical compound, but exist in bodies closely allied chemically and possessing the common property of precipitating gelatine. The "mother" substance of ellagic acid is ellagitannic acid, which is a "difficult soluble" tannin and is more susceptible to decomposition than the more soluble gallotannic acid, which is the principal tannin of chestnut wood. Ellagic acid is closely related to gallic acid into which the latter is converted on exposure to air for some time.

The chestnut tree from which tannin is obtained is known botanically as the *Castanea dentata*, and produces an annual crop of fruit which is edible. Tannin is found in the wood, bark and leaves of the tree, but the wood furnishes the best source of supply, being slightly richer than the bark and not containing as much coloring matter. Chestnut trees are not available as a source of tannin until they are at least fifteen years old, but older trees are much more desirable. The wood of chestnut trees about fifteen years old, six inches diameter, show a tannin content of approximately 7.83 percent whereas trees ninety years old, thirty inches diameter, show a tannin content in the wood of approximately 9.72 percent. The tannin content of chestnut wood differs with the location in which the trees are grown. The chestnut area in the United States is roughly within a boundary comprising Virginia, Western North Carolina, Northern Georgia and Eastern Tennessee. The wood from the Northern boundary is not as rich in tannin as that grown farther south. The tannin content of chestnut wood grown in the southern part of the belt is approximately 10 to 11 percent, whereas wood grown in the north, or

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even in the higher altitudes, shows approximately 7 to 8 percent tannin.

Chestnut wood is a coarse grained wood of intermediate hardness and durability. Its wood fibre is somewhat short and porous and it is in the pores or ducts which separate the fibres that the tannin is contained. In a cross section of well seasoned chestnut wood the tannin matter is visible to the eye. After the chestnut tree is cut down the wood is sawed into five foot lengths and split. This permits the wood to pack closer and it is allowed to remain in piles to season. This occupies six to twelve months and has an influence upon the tannin content of the wood and the drier the wood, the easier the tannin is extracted. Green or unseasoned wood showed a tannin content of 7.5 percent, whereas the seasoned wood from the same tree showed 10 percent tannin.

The preparation of chestnut wood has an important bearing upon the extraction of the tannin and it is desirable to break up the wood fibre into the smallest particles that will permit of the diffusion of the water. The economical and efficient extraction of the tannin from chestnut wood is dependent upon a number of details, which has an important influence upon the yield of extract. The influence of the various factors which enter into the operation are very fully described in a paper contributed to our Journal by C. T. Gayley (June 1920).

It is probable that tannin occurs in chestnut wood as a glucoside. In this respect chestnut wood tannin is distinguished from other wood tannin extracts and makes chestnut wood extract a most valuable agent in the tanning of heavy leather. A water extraction of chestnut wood made by the official method of analysis shows that well seasoned chestnut contains from three-quarters to one percent of glucose on the dry weight of wood. The method of extraction has a pronounced influence upon the yield of glucose—the longer the extraction of the wood is continued at a boiling temperature, the greater the yield of glucose. It would appear that the heat employed in the water extraction splits the glucose from the tannin, but whether the additional glucose is furnished at the expense of the tannin is not clearly established. Ellagitannic acid yields glucose and the hy-

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drolysis of the cellulose is a possible source of supply. A water extract of chestnut wood concentrated in vacuum on a commercial scale to 45 percent total solids shows an average of 3 percent glucose on the weight of the liquid extract. An extract of similar density obtained by lengthening the time of extraction shows an average of 12 percent glucose on the weight of the extract. The heat employed in concentrating the liquors, although the process takes place in vacuum, has the effect of increasing the glucose content of the extract. A liquid extract having 45 percent total solids and a glucose content of 3 percent when concentrated in vacuum to 95 percent total solids shows 9 percent glucose, although the purity of the extract remains the same. It is clear in this case that the increase in the sugar content of the dry extract is not obtained at the expense of the tannin, or from the cellulose. It would appear to be a product of the influence of heat upon ellagitannic acid, which splits up into ellagic acid and glucose. The ellagic acid is the insoluble portion of the "bloom", which, when deposited on the hide surface is absorbed by it and contributes to the characteristic solidity of chestnut tannages. Concentrated extracts of chestnut wood tannin on standing a few months increase in "insolubles", but analysis show less "non-tannin", so it is evident that the increase in insolubles is not at the expense of the tannin, but of the non-tannins.

Treatment of the aqueous extract of chestnut wood with a colloidal solution, such as blood albumen, precipitates ellagitannic acid with which is associated the darker coloring matters, but the glucose of ellagitannic acid is set free. There is a mutual precipitation of the two colloidal solutions, but the "tannin" precipitate, which consists of the difficult soluble tannin matter is soluble in acetic acid and is absorbed by hide powder. The removal of the ellagitannic acid by colloidal precipitation not only lightens the color, but considerably reduces the astringency of the chestnut wood and a much "mellower" tannage is produced, closely resembling an oak bark tannage. The addition of 2 or 3 percent of sodium acetate to a chestnut tanning liquor, on a 25 percent tannin basis, also reduces the astringency of the tannin and contributes to the mellowness of the tannage.

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The principal characteristic of chestnut tannin is the comparatively large percentage of glucose with which it is associated The glucose is more or less inert and is not absorbed by hide powder, but it is the source of the organic acids produced by the fermentation of the more dilute solutions of the chestnut tannin. The glucose of a chestnut wood tannin extract is contained in the "non-tannin" solution in the analytical process and consequently lowers the purity of the extract, although its presence is a desirable factor in practical tanning and should be considered in the valuation of a chestnut wood extract. The glucose is not the principal source of the production of acetic acid by fermentation which is so noticeably present in solutions of chestnut wood tannin. Acetic acid is produced as soon as the hot liquor comes in contact with the wood in the process of extraction. The condensed water from the vacuum pans employed in the process of concentrating the weak tannin infusions into extract contains from one tenth to three tenths percent of acetic acid. This condensate is more acid the more glucose is found in the concentrated extract. It is clear then, that the acetic acid is not produced at the expense of the glucose. It is probable that the acetic acid is produced by the decomposition resulting from the effect of heat in splitting the tannin glucoside molecule, with the liberation of acetic acid, or, on the other hand it may be the product of the splitting of the molecule of ellagitannic acid into ellagic acid glucose and acetic acid. When the concentrated extract is subsequently diluted for use in the tannery, it is reasonably certain that the glucose does contribute to the further production of acetic acid by fermentation. The glucose of chestnut wood tannin supplies the nutriment for the growth of moulds and fungi on the surface of the liquors and these growths are exceedingly destructive of tannin, but this can be prevented by the use of proper antiseptics. As the production of acetic acid in tannery liquors is one of the least desirable of the organic acids—its chief function being to neutralize lime rather than to plump the hide—the attention of the tannery chemist should be directed to the conversion of the glucose into lactic acid. Lactic acid is a very desirable acid in tannery liquors. It is readily absorbed by the hide and is an excellent plumping acid and contributes to the yield of leather, besides having a pronounced "mellowing" influence upon chestnut

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wood tannin. When the concentration of the extract solution is carried to the powder state by evaporation on a vacuum drying machine, all free acetic acid is completely volatilized, so that the sugars in powdered extract are readily available for conversion into lactic acid by the introduction of the lactic ferments.

The analysis of a chestnut wood tannin extract does not altogether indicate its leather forming properties. The "non-tannins" of the pyrogallol series, of which chestnut wood tannin is a type, appear to possess the quality of converting hide fibre into leather, when contact with hide fibre is of sufficient time. The contact between the hide powder and the tannin solution in the method of analysis is not sufficiently long to permit of all the leather forming properties of the solution being absorbed, although in practice the time factor has ample scope to function. It has recently been shown that gallic acid, which is present in liquid chestnut wood extract to the extent of one and one-half percent, and is contained in the non-tannin solution, is capable of converting hide fibre into leather after standing a few days.

Chestnut wood tannin when decolorized, like others of the pyrogallol class, has a more permanent color than the tannins of the catechol type, that is, they do not darken upon long exposure to light to the extent that the tannins of quebracho and hemlock, which are types of the catechol series do. A report issued by a committee of the Society of Arts, on Leather for Bookbinding (1901), condemns the use of catechol tannins for bookbinding leather, on the ground that tannages of this class deteriorate and decay with comparative rapidity. A series of tests made on the pure tannages of the chestnut wood, quebracho, oak bark, valonea and hemlock showed that the greatest tensile strength is possessed by the chestnut wood tannage.

The foregoing is a brief survey of the technical status of the chestnut wood tannin of commerce. Its commercial production involves the treatment of products from nature's laboratory, the chemical constitution of which baffles the searchlight of science. Their complexity stimulates wonder, and the pursuit of knowledge leads us ever onward, but leaves the searcher groping far behind when he undertakes to duplicate by synthesis the marvellous handiwork of nature and recalls the words of the late Joyce Kilmer.

"Poems are made by fools, like me,
But only God can make a tree."

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ABSTRACTS

A Rapid Method of Determining the Moisture Content of Wood. *Tech. Note* No. 143, *Forest Products Lab., U. S. Forest Service.* A method used by the Forest Products Laboratory for determining the amount of moisture in chips and sample borings from large pieces of wood is as follows: A specified weight of wood chips, usually 100 grams, is immersed in kerosone in a flask or retort, and the mixture is heated. The vapors are condensed and collected in a graduate. When the evaporation of moisture is complete, the oil and water are allowed to remain a few minutes until the water has all settled to the bottom of the graduate. The amount of moisture in the wood chips is then found by a direct reading. This method has been checked for accuracy with the method of weighing samples before and after oven drying, and the variations found to be less than 1 per cent.

Determination of Sulphoricinate in Tanning Extracts. By JAMET and CASTET, *Le Cuir,* 10, 90 (1921). Among the numerous means to hasten tannage is that of treating the extracts to lower the surface tension between the liquors and the hides. This accounts for the presence in some extracts of sulphonated oils generally as the sodium salt. A method is given for determining sulphoricinate which consists in treating the extract with boiling hydrochloric acid. The sulphoricinate is first decomposed into sulphoricinic acid and then into ricinic acid which is extracted and weighed. Fifty gms. of extract are gently boiled under reflux condenser with 30 cc. of 1:1 hydrochloric acid for about 50 mins. The solution is then evaporated to a paste in a porcelain dish; thoroughly mixed with 50 gms. of powdered silica and dried at 105° C. As the water evaporates the mass darkens from carbonization of the tannin by the sulphuric acid and the excess of hydrochloric acid is driven off. During drying the mass should be broken up with a stirring rod. The pulverized dried residue is extracted in at soxhlet with petroleum ether for 1½ hrs. and the extracted ricinic acid is dried at 105° C. and weighed. R. W. F.

Weak Points of Tannin Analysis. By SCHELL, *Le Cuir,* 10, 107-9 (1921). The main critlcisms of the method of tannin analysis are the principles of determination and the lack of concordant results between laboratories. There are many who would prefer replacing the present method of detanninizing with hide powder by a well defined chemical reastion which would submit tannin analysis to scientific laws. Despite innumerable suggestions offered, only one, the aluminum oxide of Wislicenus, would appear to hold out any hope and unfortunately it has not been possible to obtain this reagent sufficiently homogenous and in sufficient quantity. Since the present complex and insufficiently precise hide powder method must be used it is absolutely necessary to rigidly standardize and control it for concordant results. For soluble solids the term "optically clear" is not definite, it having been shown (*Le Ciur,* 10,57) that entirely different

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figures can be obtained from solutions meeting this requirement. The porous filter thimble should be condemned as in obtaining a sufficiently clear solution the insoluble figure is exaggerated. It also frequently influences the color readings making it necessary to resort to other means of filtration for the latter measurement. The filtration for soluble solids should be carefully standardized and logically the same method should be used for both analysis and color readings. Standardization of the hide powder has already proved helpful in reducing variations, although disconcerting differences still occur. All chemicals used in the analysis such as the chromium chloride, kaolin, distilled water, and so on, should be standardized. When the entire method of tannin analysis is outlined in detail and a uniform method rigidly adhered to, it is believed that discordant analyses will seldom occur. R. W. F.

Mineral Tannage III. By W. MOELLER, *Coll.*, 608,552 (1921). The influence of time, volume and concentration on the adsorption of chrome alum by hide powder was investigated. In one series of experiments with a small volume of solution, 100 cc. portions of solutions of chrome alum having strengths of about 1%, 3% and 5%, and 100 cc. portions of basic chrome alum solutions containing about 0.9, 2.1; 2.8 and 3.8 grams of CrO_3, were added to 4.4 gram portions of hide powder and allowed to stand for varying times. At the end of 1, 3 and 8 days and 1 and 3 months a solution of each strength was filtered off and analyzed for chromium content and hydrolyzed hide substance. Another series of experiments with large volumes was also carried out. One liter portions of solutions of chrome alum and of basic chrome alum, containing about 1 and about 3 grams of Cr_2O_3 per 100 cc., were added to 4.4 gram portions of hide powder and analyzed at the end of one day and one month. Experiments in which the liquor and hide powder are allowed to stand for a longer time are not complete. No maximum adsorption of chrome was found as was the case in the work of Thomas, Kelly and Baldwin (THIS JOUR., 15, 147 and 487 (1920). The results agree with those of other workers except that the basic chrome alum in the large volume was adsorbed to the extent of 37.25% (parts Cr_2O_3 per 100 parts hide powder), from the dilute and 48.19% from the concentrated solution. This is a much greater adsorption than has previously been considered possible. The author concludes that the amount of Cr_2O_3 taken up depends in a very great degree on the volume of the solution and the time. The time factor has only a small influence when the volume is small but a great influence when the volume is large. No end point or equilibrium in the adsorption was reached in these experiments and therefore does not exist. Since all methods of tanning are similar there is therefore never an equilibrium between any tanning material and hide, but an endless adsorption. The apparent end point in the adsorption of any tannin is caused by a disturbance of the necessary peptisation condition in the tanning solution. As soon as this condition is restored the adsorption proceeds. With an unlimited volume independent of

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the concentration and in an unlimited time there is no limit to the amount of tanning material which will be adsorbed. Neutral chromium salts do not prevent hydrolysis of the hide but hydrolysis proceeds hand in hand with the adsorption. Chromium salts without the addition of alkali are therefore not tanning matter. They are partially dissociated by the hide and changed to incomplete tanning systems but are essentially acids. True tanning liquors are obtained by adding alkali to chrome alum solutions until a permanent precipitate just forms for hide does not hydrolyze in these solutions more than in distilled water. I. D. C.

The Choice of Methods for Chrome Tanning. By B. KOHNSTEIN, *Haute und Lederberichte*, 1920, No. 16, thru *Coll.*, 608, 584 (1920). The choice between the one and two bath processes usually depends on the price and possibility of obtaining the chemicals, but for certain kinds of leather only one process is suitable. The sulfur which forms in the two bath process is desirable for certain kinds of leather, while for others where the sulfur corrodes the apparatus or hinders finishing, it is undesirable. However, the sulfur deposit can be eliminated by using sodium bisulfite instead of sodium thiosulfate. Several examples are given in which one process or the other is preferable.

Harness leather is usually tanned by the one bath process since this leather does not wrinkle easily and there is no sulfer to corrode the buckles and other metal parts. Leather containing sulfur will stand a high degree of heat and can also be vulcanized to rubber. In one case the author observed lawn tennis shoes made of two bath chrome leather and dusted over with a white pigment which turned dark after a short storage. Examination revealed the presence of white lead in the pigment and this had been changed by the sulfur to black lead sulfide. Sulfur is very undesirable if the leather is to be ironed hot or glazed, for the heat causes the sulfur to sublime onto the surface where it forms a gray deposit. For the same reason, leather containing much sulfur is not suitable for patent leather since the sulfur causes a dull finish. Chrome leather, which is to be colored, should not contain sulfur since the sulfur collects in the wrinkles and hinders or prevents the taking up of the dye and so causes uneven dyeing. In retanning glove leather and also lately for chamois leather, the one bath process is always used if the leather is to be dyed. I. D. C.

Tanning Skins with the Hair On—Furs. By B. KOHNSTEIN, *Haute und Lederberichte*, 1920, No. 19, thru *Coll.*, 608, p. 581 (1920). Furs must first be cleaned free from dirt and blood and the connective tissue adhering to the under side of the skin removed. Valuable furs must be dried carefully or putrefaction and heating will occur causing a loosening of the hair or an undesirable change in the color or quality of the hair. Softening of valuable furs must not be done by dipping into and working in water, but by covering the outspread skin with a paste made of pine sawdust and three percent salt solution. This not only softens the skin, removes blood

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and hinders putrefaction but also prevents matting and curling of the hair. This treatment with the paste is repeated until the desired softening is obtained. Ordinary furs are softened by soaking in water, to which in summer 1½ per cent. of salt has been added. They are then placed for 1-2 days in running water with the flesh side up, but never hair to hair or heating will occur. After removing the water in a centrifuge the fat and connective tissue are removed by hand or machine. The further treatment depends on the use to which the fur is to be put and on whether the fur is to be dyed artificially or in imitation of some other animal skin. Marten, filchet and fox skins were formerly tanned by rubbing a lard-like fat into the flesh side, rolling up the skins with the hair sides together and working the skins in this condition with the bare feet. The skins were then spread out with the flesh side up and left for several days after rubbing on a mixture of bran and salt. The skins were next fleshed, treated again with salt and bran, and after a short time hung to dry over ropes with the hair side in. The skins were now moistened with salt water, stretched and softened, rubbed on the flesh side with an emulsion of olive oil, egg yolk, water and meal and that worked in dry sawdust in a treadmill at 25°C. with the bare feet. Finally they were degreased with warm quartz sand or gypsum in a treadmill. The above treatment is essentially a pickling with fatty acids or sour bran, therefore with lactic acid and salt. Often at this point, and especially with lambskins, a pickle of salt and sulfuric acid is used. For example 400 small lamb skins are moistened with a mixture of 100 kilograms of salt, 1½ liters of sulfuric acid and 20 kg. of bran and piled with the hair side out for 6-8 days, moving and working occasionally. Then they are pressed in a centrifuge, hung to dry with the flesh side out, and left in the storehouse for some time for the tannage to fix. This pickling gives a thin light fur which is more suitable for dyeing than an alum-salt tanned one. Chinese furs, which are famous for their flexibility and softness, are tanned similar to our glove leather except that fish spawn is used instead of egg yolk. For 100 kg. of wet fur use 10 kg. of meal and 3 egg yolks stirred with 10 liters of water and 7 kg. of alum and 2 kg. of salt stirred with 10 liters of water. These two mixtures are poured together and rubbed into the flesh side. Then the skins are placed in wooden vats with the flesh sides together and the rubbing with the tanning mixture repeated. To prevent crystallization of the alum, add glycerine or tartar, 5 kg. of iron free alum, 1½ kg. of salt and 1 kg. of tartar are dissolved in 10 liters of water and 1 liter of commercial glycerine is added. In France the alum is partially replaced by aluminum acetate for this gives a fur which is only slightly hygroscopic and one from which the salts do not readily crystallize. Also the tanning matter is less easily washed out. I. D. C.

Emergency Tannage (Notgerburg) and Leather Quality. By W. EITNER. *Haute und Lederbedichte*, 1920 No. 13, thru *Coll.*, 608, p. 580. There was a decrease in the tensile strength of belting leather when the tanning process was modified during the war. The causes for this de-

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crease were first the fact that the leather was not tanned through due to unsuitable tannage and the wrong use of cellulose extract and also due to stuffing at too high a temperature and stuffing with mineral grease to which pitch had been added. The author describes the tanning of belting leather with a mixture of native pine bark and cellulose extract. The hides are first tanned in a series of ten vats containing a liquor made by mixing the old liquor from the lay aways with used extract from the drums. They remain in each vat three days and are then drummed in a liquor made by hot leaching fresh pine bark and adding cellulose extract. The cellulose extract aids in the solution of the difficultly soluble parts of the pine liquor.The drumming should be for 10-12 hours at a temperature below 30° C. and in a liquor equal to but not over 8° Bé. The hides are next piled and left for 2-3 days, then placed in lay-aways with coarsely ground pine bark and a liquor made of concentrated fresh pine extract and enough cellulose extract to give a strength when cool of 35° Bé. At least four weeks are required in the lay-aways and heavy butts require a second period in the lay-aways. This process can be used for sole leather by using liquors 2° or 3° Bé stronger than for the corresponding weight of belting leather. The leather is stuffed hot and mineral grease is added to the fat in case the latter is not soft enough. I. D. C.

Aldehyde-Tannage VI. By W. MOELLER, *Coll.*, 609, 20-31 (1921). In the previous work a moderate concentration of formaldehyde was used and a small volume of solution, but experiments with other tannins showed that the volume and time were very important so investigation was made of the adsorption of formaldehyde from a large volume of dilute formaldehyde and from a small volume of concentrated formaldehyde. In the first series of experiments 4.4 gm. portions of hide powder were treated with 1000 cc. portions of N/10, N/2 and N formaldehyde solutions and the amount of formaldehyde absorbed was determined after 1, 8 and 14 days. The series was then repeated using a neutralized instead of ordinary formaldehyde. The adsorption of ordinary formaldehyde increased regularly with the time and had not reached equilibrium after 14 days. The greatest adsorption was from the normal solution and amounted to 14.5%, based on the weight of the hide powder. The adsorption of the neutralized formaldehyde was much less than that of the ordinary. Also less of the neutralized formaldehyde was adsorbed from the normal solution than from the half-normal. The adsorption from the normal solution had decreased to zero in 8 days but increased again in 14 days. This latter apparent increase was due to the loss of formaldehyde through the Cannizzaro transformation. There is also some polymerization in the alkaline solution. Methyleneamino acids are also formed by the action of formaldehyde on the decomposition products of the hide and these acids have a hydrolyzing action on the hide powder. This was shown by the fact that the dissolved hide substance amounted to 2% or 2.5% instead of 1.75% as is the case when th hide powder is treated with pure water. The action of these acids is very slow but

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if they are not washed out they will cause brittle grain in the leather after storage. For the experiments using a small volume of solution 4.4 gram portions of hide powder were treated with 100 cc. portions of 15% and of 30% formaldehyde for 1, 8 and 14 days. Both ordinary and neutralized formaldehyde were used. In 14 days the hide powder had adsorbed 24.46% of the ordinary formaldehyde, a much greater adsorption than had previously been considered possible. Even then equilibrium had not been reached and adsorption would apparently have continued if the time had been increased. Less of the neutralized formaldehyde was adsorbed, 12.75% being the maximum, but again there was no evidence that the adsorption was approaching a limit. Less hide substance was dissolved in these concentrated solutions than in the dilute solutions in spite of the greater concentration of methyleneamino acids. To determine which leather was more stable the various portions of hide powder which has been treated with formaldehyde for 14 days were allowed to stand with 100 cc. water, first for 3, then 8 and finally 30 days. The water was filtered off after each time interval and the amount of formaldehyde and hide substance in solution was determined. The amount of hide substance washed out was quite constant for all concentrations, volumes and time intervals; and was approximately 0.5%. Much more formaldehyde was washed from the hide powder which had been treated with concentrated than from that treated with dilute formaldehyde. Also more was washed from the hide powder treated with neutralized than from that treated with ordinary formaldehyde and this difference was much greater in the case of the hide powder treated with dilute formaldehyde. Therefore tanning with neutral formaldehyde solutions should be less advantageous and give a less stable leather than tanning in acid, or at least in formic acid solution. But in the literature and patents neutral or slightly alkaline formaldehyde is recommended. Neutral formaldehyde, although adsorbed to a less extent, therefore seems to be able to give the desired properties to the leather and the absolute amount adsorbed is not important. I. D. C.

Note on the Cause of Gas Formation in Oak Tannin Extracts. By F. LIEBERT, *Coll.*, 610 76-7 (1921). An examination was made of several strongly fermenting extracts containing from 16.7 to 22% of tannin and from 67.7 to 52% water. The odor of these extracts resembled that of fruit esters indicating that yeasts were the cause of the fermentation. Yeasts could not be detected directly in the extract but by inoculating malt extract-gelatine plates with the fermenting extract a growth of pure yeast resembling *saccharomyces apiculatus* was obtained after two days at 22°C. No molds or bacteria developed. Since concentrated tannin solutions are very poisonous for protoplasm the yeast cell walls must entirely prevent the entrance of tannin into the cell. From 9.4 to 22.1% of nontannin was present and it was probably partially segregated but it could not be determined whether the yeast developed in the nontannin only or in the entire extract. The yeast dropped from the air into the extract during cooling in the mixing vats and its presence in the extract can be prevented by first disinfecting the vats with sulfur dioxide and then keeping them covered. I. D. C.

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PRESIDENTIAL ADDRESS TO THE EIGHTEENTH ANNUAL MEETING

By F. H. Small

A perusal of the opening addresses of the past Presidents of our Association,—if one has the courage to tackle such a task,—will show that they range from grave to gay, from serious to sentimental, from discursive to didactic, from interesting to instructive, that in short they establish no particular precedent for opening addresses. Your President in compounding his message of greeting may therefore feel free of any fear that he is not maintaining the traditions of the office. I pass on this word of cheer to my successors, because after mulling over the things which ought to be said it occured to me to see whether they fell within the requirements and I undertook what proved to be the pleasant recreation of reading these past Presidential addresses. The one disturbing result of my reading was that I discovered that many of the words of wisdom I was preparing to utter, the sage advice I was intending to offer, already had constituted the basic themes of the talks of numerous of my predecessors. This was disconcerting, but inasmuch as the necessity of the saying was not lessened by the having-been-said I shall proceed to inflict some of these thoughts upon you, hoping that they may have novelty of expression if not of fundamental idea. In general, I shall try to give you in brief outline an account of some of the happenings in the affairs of our Association during the past year, and of some suggestions for the future that seem deducible from them.

Let us start with finance. These are days of upsets, days when business customs are reputed to have altered and not always for the better, but through all the changes a requisite for continued conduct of business seems still to be solvency, ability to meet obligations. During this past year our Association has faced a situation where it has borrowed the limit on its Liberty Bond investments and has been glad to accept a loan from one of its good friends in order that it might pay its current bills. This situation arose from the fact that for some time past the expenses of our Association steadily have increased and its revenue has failed to keep equal pace. Our revenue is derived from two sources, membership dues and our JOURNAL, its sale and adver-

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tising. Long study showed no escape from the conclusion that if you have only two sources of revenue and you must have more revenue it is necessary to increase the amount derived either from one or the other, or from both sources. Your Council in its discussion of how best to remedy the financial situation decided to compromise and try both. The membership dues were raised, the advertising charges raised, and a special drive made to secure both members and advertising. The increase in membership dues was decided upon most grudgingly as we wished to extend the privileges of our Association to all qualified. We realized that these were days of economy and that some at least of our members would find the increase a hardship. However, there seemed no escape from the necessity of increasing them for the present at least,—hence the decision. I am extremely gratified to be able to report that our members stayed with us most loyally, that only thirty members resigned altogether and of these only 17 members resigned specifically because of the increase in dues. There are to-day 177 active, 230 associate and 99 mutual, or a total of 506 members in our Association as against 152 active, 211 associate and 45 mutual, or a total of 408 members a year ago, which I submit as a thoroughly satisfactory showing and one in which we may feel justifiable pride under the circumstances. The effort made to secure new advertising also met with good response. Our advertising pages have increased from 16 in the May 1920 JOURNAL to 24 in the May 1921 JOURNAL, or an increase of 50 per cent and this in spite of the increased rate which we felt justified in asking. We all are indebted to those members who gave so freely of their time in accomplishing this happy result and in particular I wish to record my personal gratification at the whole-hearted and generous way in which our tanner friends responded to our appeal for assistance through the use of the advertising pages of our JOURNAL.

If we maintain our present membership and our present volume of advertising, we shall be able to do somewhat better than meet the running expenses of our Association as they are to-day. If we can increase either or both it may make possible a reduction in our present membership dues, probably not to the former $5.00 but perhaps to the former half-way mark and the officers of the Association believe this most desirable. There still are many

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persons interested in leather from some angle who are not members of our Association. There are many who might profit from the use of our advertising pages who are not now using them. If you believe with your officers that our membership dues ought to come down, why,—get busy.

Mature consideration led to the belief that although it meant increased expenditure, efficient conduct of the affairs of our Association required that the burden of detail under which the Secretary and Editor had been laboring, should be shifted to the shoulders of someone paid to carry it. As our Association had grown, the volume of business detail demanded of these officers had grown also until in recent years it had become a most onerous burden. Your Council, realizing the necessity, created the paid office of Executive Secretary, the incumbent of which should handle the detail of the Secretary-Treasurer's office and that of the business of the JOURNAL. We feel that the course of events has justified our action. Our Association was most fortunate in the young lady who was found to fill the office and her competant handling of the above-mentioned details as they were entrusted to her has aided greatly in accomplishing the adequate and economical administration of the affairs of the Association during these trying times.

The volume of committee work carried on during the year has been rather above normal. It well might have been more save that the prevailing business depression and resulting depleted laboratory staffs have limited the possibilities of committee research. Much of the work has been of unusual interest and seems likely to prove far-reaching in its possibilities for progress —and there never was a time when we so needed to look to our laurels in maintaining a high quantity and quality of research as the present, if we are to keep our country in the running in the efficient and scientific production of leather. Our colleagues in the Society of Leather Trades' Chemists are rapidly recovering from the paralysis of laboratory research caused by the war and their *Journal* is once again beginning to be filled with accounts of most admirable studies. If reports be true, Germany is preparing to call to her aid in her study of leather-making one at least of the best known and ablest chemists in the scientific world

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to-day. It is some comfort to know that in this country the valuable researches which have been carried on at Columbia under the Gallun grant are being continued, and it certainly has been a great source of satisfaction to us all that the Tanners' Council, during the past year, has located its Research Laboratory at the University of Cincinnati, with one of our members in charge as Director of Research. The University authorities are taking a keen interest in the success of the Leather Research Laboratory; the Director is promised and is receiving the help of the very able staff of the University, and with this assistance and the ability of the Director we may confidently look forward to results of great value.

This, however, in no way relieves our Association of its duty in the circumstance. We must do our part. Committee work is the foundation on which our Association was built. It may not be an ideal mode of study. It may not be able to replace individual research, to compete with it in sustained effort or equal it in brilliancy, but through committee work we can secure the combined effort of many minds and this makes possible no mean degree of accomplishment. Many of our members are losing a rather wonderful opportunity for training and development through their failure to participate in the committee work of the Association. A mere absorber of knowledge is of no great value to himself or anyone else.

A good friend of mine, in urging that now is the time for the chemists of our industry to get busy and do their part in keeping leather-making in this country at the forefront for efficiency and quality, wrote me, "The chemist has surrounded himself with an atmosphere of mystery which has tended to create misunderstanding and frequently complete misapprehension of the functions and extraordinary value of the chemist." We had thought we were reasonably frank and above-board. At least we now are here on exhibition, open for inspection and criticism. At some of our former meetings we have been privileged to have a few of our tanner friends present who have participated in our discussions. We are expecting to have some of the practical men of the industry with us at this meeting. We welcome them. We hope that they will find something of interest and of

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value to carry away from our meeting and that they will feel entirely free to take an active part in our deliberations and to give us the benefit of any suggestions looking to an increased usefulness of our Association. We have no interest in any enshrouding veil of mystery. We cannot always use fifty words to say what may be said in one, merely because the one happens to be a technical term not familiar to the layman. That is not efficiency. But we do wish to make so clear that he who runs may read, the possibilities and the accomplishments of the chemists' part in the making of leather, and if we are not doing this we are ready to reform. One of our number who was a splendid example of ability to interpret the chemist to the layman from an intimate understanding of both has been lost to us this past year. John H. Yocum, the originator of our present shake method of tannin analysis, a charter member, a sturdy and efficient worker for our Association and our Industry has passed on. We miss him.

A Presidential address would fail of being one were mention neglected of our JOURNAL. Your President is mighty glad that this is so. He welcomes the opportunity to express publicly his appreciation of the able efforts of the Editor and his assistant in the preparation of the JOURNAL, and his satisfaction with the quality they have maintained. The Editor deserves better treatment at our hands than he receives and it will be a happy day for him when he is under the necessity of turning down contributions for lack of space instead of having to spend valuable time trying to inveigle some unwilling soul into writing a potboiler.

This has been a trying year for the business man and by reflection, for his chemist. The leather chemist has had a new set of problems to face, problems connected with economic curtailment of production rather than of more speedy and enlarged. Such problems while interesting fail of being exhilarating. Sentiment is rapidly gaining ground that the turn has come, that business is improving, but the day of wasteful and extravagant production has passed and we may hope for good and all. Our Association has its part to perform in these days of reconstruction. Let us each do our bit to ensure that it plays its part well.

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THE SOAKING AND LIMING OF HIDES.*

By C. M. Morrison

This is a very old subject of which I know but little and it is not my intention to bring any innovation to you regarding this process, but, rather to discuss present day methods as I see them.

The soaking and liming process is so well understood by all heavy leather tanners that it would be impossible to say anything that would add to their store of knowledge on this subject. But a full and open discussion might lead to the uncovering of many points that would be of vital interest to the entire industry. In many ways, I believe that we are following the same general lines that were followed centuries ago, with added improvements here and there, such as shortening the time by the economical use of materials, the employment of machinery, etc.

The soaking of hides is the first process it goes through in order to prepare it for tanning, and it seems almost foolish to try to tell an intelligent body of men, such as you are, why and how it should be done. However, the object is to bring it back as near as possible to the condition it was in when it left the animal's back. To do this, it must be soaked until all the fibers have been softened, cells and voids all opened up. This is accomplished by putting back into the hide the moisture that has evaporated in the curing and storing of same. The usual method for soaking green salted hides, is to first wash them in a revolving wheel or drum, with a good flow of water to free them of all salt, manure and dirt. The time required for washing them in the wheel usually runs from five to ten minutes, depending on the cleaning required. The flow of water available for this purpose is also quite a factor. Hides piled in the hide house for any length of time will get hard and dry along the folds, if they are left in bundle condition, the washing in the wheel will soften these spots and aid in a more uniform soaking. If they become quite dry and hard along the folds, a good plan is to wet them up in bundle condition a few hours before placing them in the wash wheel, as often damage is sustained on the grain of the

* Read at the Eighteenth Annual Meeting at Atlantic City, June 9, 1921.

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hide in these dry hard spots by the vigorous handling they are subject to. After washing in the wheel, the soaking is completed by either hanging them in the soak vats over sticks or toggling together and reeling them in one on top of the other.

The washing of green salted hides in a revolving wheel has been a source of much discussion among tanners, especially as to the loss of hide substance by so doing. I have known wash wheels or drums to be installed and after a short time thrown out, later to be re-installed permanently. In the way of comparison, I have run many tests by weighing up packs of hides from the same car, soaking one pack by hanging in the soak vats over sticks, running the other pack in the wash wheel, then toggle together and complete the soaking by reeling them in one on the top of the other, with a final result always in favor of the washed hides. But upon entering most any beam shop to-day and seeing the amount of hide substance being trimmed off and thrown into glue stock, one would be inclined to think that loss of hide substance was a dead issue. Some of the advantages gained in washing hides, is a more even uniform soaking, keeping cleaner soak and lime baths, thereby getting better results from the quantity of lime and materials used. The soaking of a hide is very important if the best leather possible is to be obtained, and at this point I wish to submit some small pieces of leather showing the results of insufficient soaking. The pit marks represent portions of the hide where the fibers have not been released from the dry dead condition before going into the limes.

The quality as well as the quantity of water available is one of the most essential things used to assure the success and prosperity of any tannery. It also spares the tanner many sleepless nights. I recall having been employed several years ago at a tannery using river water for soaking and it required very close application to handle the hides in such a way that would prevent damage during the extreme hot weather when the water would warm up to about 85 degrees. At such a season as this our soaking time was reduced to eight hours. The length of time required for soaking green salted hides is governed largely by the kind of water available, varying from one to three days. A good well water is desirable for this purpose owing to the water

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coming from the well at practically the same temperature all the year, which makes the control of soaking less difficult. Time required for the soaking of dry hides is very much longer than green salted, as the moisture content of this grade of hide is very low when it reaches the tanner. Instead of using the revolving wheel or drum for breaking up and softening the hide. the Hide Mill or what is commonly known as "The Knicker" is used in the first operation of softening and breaking up the hide, completing the soaking in the usual way.

After the hides are brought to the desired condition by soaking they are passed on to the lime baths. These are arranged in series to meet the individual requirements. The length of time required in the lime baths varies from 2 to 5 days, depending altogether on the kind of leather produced, and the individual method of handling. However, I believe that the majority of heavy leather tanners take about four days for this process, handling the hides each day. Usually, tanners using the two or three day method, do so by frequent handling of stock, two and sometimes three times each day, and finish up with a warm water bath, and in many instances heating up the last lime bath. Tanners using the four day method of liming usually employ all cold limes and finish up by putting the hides in a warm water bath for a few hours prior to going to the unhairing machine. The employment of heat in the last lime bath, especially in extreme cold weather, when the temperatures of all the baths are running low, and the action of the lime on the hair cells very slow, is a life saver for the beam shop foreman. It enables him to get out his day's work on time and keeps his workmen in good humor.

We, must not, however, lose sight of the fact that the employment of heat in connection with hide substance is a very dangerous proposition, and without being handled with care and watched diligently great damage may be sustained in a very short space of time. The quantity of lime required varies according to the kind and quality used. Referring back to my memorandum book, I find that the amount used in different shops runs from three to seven pounds per one hundred pounds of hides. The wide differential being caused by the quality and process

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used. The shop using the quick process, by frequently handling of hides and warming up the last lime and water bath use less than the shop using all cold baths and handling only once each day.

Sulphide of sodium is widely used in conjunction with lime to loosen the hair, and the amount of sulphide used affects the quantity of lime required to give the desired results. The use of sulphide in conjunction with lime is an interesting question, and has been the source of much discussion among tanners. Too liberal use will throw a heavy coarse grain on the leather produced, also cause the hair to split and pulp, making it unsalable. The removal of hair with the use of sulphide alone can be accomplished very quickly, and experiments have been carried on by many tanners, with some degree of success, however, I know of no one who has adopted the method.

Not many years ago it was customary to clean the lime vats every five or six weeks, and it was nothing unusual to see lime deposit twelve to eighteen inches deep in the bottom of the vats. The introduction of chemistry in the tanning industry taught the tanner that a condition of this kind was not conducive to preservation of hide substance. Ammonia, an enemy of the tanner, especially at this point of operation, is created very fast under a condition of this kind. I have actually known the fumes to be so bad that the workmen could not stand to work over the pits long at a time, and had the modern gas mask been invented 25 years ago, am sure we would have seen them employed by the workmen at this point of operation. However, in all well regulated shops you will now find the soaks cleaned each day and the limes every ten days or two weeks, especially during the warm season, which makes it possible for the workmen to survive without the use of a gas mask.

Not many years ago, all tanners used lump lime which had to be handled with care in the slaking tub or the mixer in order to prevent burning the lime and to get it thoroughly slaked. Today, however, we have hydrated lime, which I believe is being used by a majority of tanners. To my mind, the introduction of hydrated lime has been one of the big advances of recent years in materials used in the beam shop. Most any shop foreman can recall the day of lump lime, and how careful he had

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to be, in order to prevent lime burns on his hides. By the use of hydrated lime this worry is entirely eliminated, as I have yet to see a hide burnt when it is used.

I shall not enter into the chemical content of lime which should be used, other than to say that the quality plays a very important part as to the amount used to obtain the desired results. Any lime will swell the hide, attacking the hair root cells and loosening them, but lime carrying a high percentage of magnesium oxide will not swell and plump the hide like one composed largely of calcium oxide. A good, sharp, clean lime bath is the desired condition, regardless of the kind of lime used. It is also very important that the lime baths be thoroughly plunged or mixed before the hides are placed in them; an ideal way to do this is with compressed air if available. To my mind this is one of the weak spots in the modern beam shop as it is so very easy to neglect this important operation.

After the hides have completed the soaking and liming processes they are passed on to the unhairing and fleshing machines, and here the defects of the liming and soaking operation will show up to a large extent, which will at once be observed by the foreman or the tanner in charge, provided they have not reached the state of seeing things until they do not see them.

FURTHER OBSERVATIONS ON THE WILSON-KERN METHOD OF TANNIN ANALYSIS.*

By G. W. Schultz

In a previous paper[1] summarizing some observations on the proposed method of Wilson and Kern for tannin analysis it was demonstrated that it is practically impossible to determine the amount of tannin removed by hide powder from a solution of tanning material and which remains combined with it after washing, principally because of the varying nature of the samples of hide powder and because of the heterogeneity of the samples of

* Presented at the Eighteenth Annual Meeting at Atlantic City, June 10, 1921.

[1] G. W. Schultz and T. Blackadder, This JOUR. 15, 654 (1920).

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air dry tanned powder. It was shown that the fine particles of tanned powder which passed through the cloth when squeezing out the aqueous solution contained a much higher proportion of tannin to hide substance than any fraction of the powder that remained in the cloth which comprised the sample to be analyzed and on which the computations were based. It was also shown that the air dried tanned powder could be roughly divided into three fractions, these fractions varying widely one from the other in the amount of tannin they contained per unit of hide substance. If the first fault could be corrected by washing in an alundum thimble as the authors suggest we would still have the latter to contend with, slightly augmented by a greater amount of dust-like material. Anyone who is familiar with sampling and analyzing a material consisting of a mixture of powder and fiber, such as divi divi for instance, will readily perceive, that to obtain an average analysis of such samples as represented by these tanned powders, especially by the use of the small amounts necessary for analysis, is almost impossible and at the least impracticable. The error introduced by analyzing the tanned powder is in my opinion the cause for a large portion of the difference between the Official Method and the method of Wilson and Kern which was ascribed to error in the Official Method.

Aside from this it was demonstrated that by reconcentrating the detannized solution and washings from several determinations by this method and treating with a fresh portion of hide powder a certain amount of material combined with the hide which is resistant to washing and which we claimed as proof of the presence of tannin remaining in these solutions after the treatment prescribed. Wilson and Kern in a second paper on their new method[2] confirm these findings but claim that what is found here is non-tanning material that has been converted into tannin by the boiling involved in the reconcentration. In the course of further work on this method the writer has reconfirmed the results mentioned and it is hoped, has established conclusively that there is a certain amount of material in the detannized solution and washings from a determination according to the Wilson and Kern method which material will combine with the

[2] The Nature of Hide-Tannin Compound and Its Bearing Upon Tannin Analysis. This JOUR, 16, 75 (1921).

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hide powder and be resistant to washing as can be demonstrated by adding hide powder to the washings from several determinations without concentrating them.

A set of nine determinations was made using 200 cc. of a solution of liquid chestnut extract containing 36 grams per liter, 12 grams of hide powder were added to each and shaken six hours after which they were washed fifteen times. The detannized solutions and first washings from these were collected and combined, filtered until a sparkling, clear filtrate was obtained, 12 grams of air dry hide powder added to this and the whole shaken for six hours. The second third and fourth washings were also collected, filtered and treated in the same manner with 12 grams of hide powder. The aqueous solutions were strained through a linen cloth and the powders were washed 15 times with 200 cc. distilled water, air dried and analyzed when the following results were obtained:

	Moisture	Grease	Ash	Hide substance	Tannin	Tannin per 100 hide substance	Per cent tannin for a single determination
Detannized solution and 1st washing	12.54	0.77	0.21	81.46	5.02	6.16	0.90
2nd, 3rd and 4th washing	12.67	0.70	0.17	83.31	3.15	3.78	0.55

Such results show beyond a doubt that there is tannin in the detannized solution and wash waters after the treatment prescribed by the authors and it is safe to assume that the amount present far exceeds the amount indicated here not only because all of the washings were not treated and because of the errors inherent in this method of determining tannin as pointed out previously but also because of the fact that all of the tannin is not removed from these solutions even with the second application of hide powder as can be demonstrated by the following experiment with a quebracho solution:

Seven 200 cc. portions of a quebracho solution containing 18 grams of solid extract per liter were treated in the same manner as the chestnut solutions. The consecutive washings were collected and filtered free from all suspended matter. The total amount of solution was slightly over 22 liters. To six liters of this solution, which comprised the original detannized solutions,

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the first three washings and a part of the fourth of all seven determinations, in an eight liter bottle, 12 grams of hide powder were added and the whole shaken four hours. The solution was then strained through a cloth, the hide squeezed and placed back into the same bottle when another six liters of the washings were added and the same procedure repeated until the powder had passed through all of the washings. The total time of shaking was 16 hours. To the solutions as they were squeezed from the above a second 12-gram portion of hide powder was added and treated in the same manner as the first. These two samples of hide powder, after washing 15 times and air drying, analyzed as follows:

Hide powder No.	Moisture	Grease	Ash	Hide substance	Tannin	Tannin per 100 hide substance	Per cent tannin per each determination
1	11.63	0.43	0.15	82.47	5.32	6.45	2.65
2	12.73	0.50	0.11	82.30	4.36	5.30	.2.18

Here it will be seen that whereas the first hide powder passing through the wash waters removed at least 2.65 per cent tannin, calculated on the weight of original extract, the second portion of hide powder removes slightly less or at least 2.18 per cent. Thus it is seen that treatment of the wash waters with two successive portions of hide powder of 12 grams each removes at the least enough tannin to represent 4.8 per cent of the extract from a solution that gives no test for tannin with the gelatin-salt reagent. Moreover, there has been no possible chance of it being formed from non-tannin matter.

As a reason for the statement that tannin was formed from non-tannins by boiling, Wilson and Kern state that when the wash waters were concentrated and diluted back to the original volume they gave a precipitate with gelatin-salt which was not the case originally. The writer has confirmed these findings and such was found to be the case even by concentrating in vacuo. Another point worthy of mentioning at this point is the fact that, although the wash waters were always filtered until sparkling clear before concentrating, after they were concentrated to a volume of 200 cc. they contained very much insoluble sus-

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pended matter[3]. In continuation of these experiments, 200 cc. of a solution of chestnut extract containing 36 grams per liter, were diluted to 8 liters. My gelatin-salt reagent gave no test for tannin after filtering a portion of this solution. This 8 liters of solution evaporated to 200 cc. and diluted back to 8 liters gave a decided reaction with gelatin-salt, *but when this solution* together with more of the same dilution *was concentrated to a syrupy thickness and then diluted back to the original volume gelatin-salt no longer gave a reaction for tannin; neither did the insolubles appear more than usual.* Such does not seem to indicate that the formation of a precipitate with gelatin-salt in the partially concentrated solutions after diluting back can be attributed to a "valuable property of non-tannins" or that a chemical change has taken place. It is hardly probable that non-tannins, after being converted into tannin by a "chemical change" by concentrating to a certain point, will be reverted into non-tannin after continuing the concentration only a little further. A plausible explanation for the phenomenon may lie in the assumption of a change of state of the tannin originally present in the solution. It is highly probable that tannin at such a great dilution is in true solution and when molecularly dispersed it is incapable of precipitating gelatin from solution. When subjected to prolonged heating in concentrating, it is probable that the power of tannin to associate and pass within the colloid realm is augmented so that when such a solution is diluted back it is likely we have a coarser degree of dispersion or at least a system which contains more colloid particles than the original and the assumption follows that tannin in the colloid state *only* precipitates gelatin from solution. When concentrated to a syrupy liquid it is possible that the tannin is brought to its original state, possibly by peptization, so that when the dilution is carried out again it forms a molecular dispersion. The formation of considerable insolubles as pointed out above tends to confirm the assumption of association caused by the high temperature where the formation of tannin aggregates has proceeded until some of the particles have passed colloid dimensions. Hence in lieu of the findings reported above, and the fact that Wilson and Kern found nearly as much tannin in the concentrated wash

[3] See also this JOUR. 15, p. 661, footnote to Table III-A.

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waters from a determination with Gambier extract as they found in the original solution, the absolute worthlessness of the method, under the conditions prescribed by the authors to obtain the results claimed for it, is self-evident.

Since it has been proven, at least to the writer's satisfaction, that nothing definite can be obtained as to the amount of material removed from a given solution that remains fixed by the hide powder after washing, through an analysis of the powder that remains after such operations, it was decided to collect all of the washings and determine the soluble matter in them. Then by ignoring the insolubles, as was done in the original method, and deducting the amount of soluble solids in the combined detannized solution and washings from the total solids of the original solution, the difference can be called the amount of tannin fixed by the hide powder under the conditions employed. This method was employed so as to obtain some comparable results to definitely establish the relation between the Official Method and that of Wilson and Kern. Since Wilson's principle reason for condemning the Official Method was due to the fact that an increasing curve was obtained by increasing the amount of hide powder which he claims is due entirely to increased absorption of non-tannins, a comparison was made of the two methods under identical conditions as to the solution, volume, concentration and temperature, amount of hide powder and time of shaking, for five different amounts of hide powder, and for two different kinds of tanning material. The *modus operandi* was as follows:—
4 liters of a solution containing 12 grams per liter, of liquid chestnut extract was prepared by dissolving in hot water, standing over night and making up to volume in the morning. 200 cc. of this solution was pipetted into each of 15 shaker bottles which were divided into 5 groups of 3 each. Into each of the first three an accurately weighed amount of 2 grams of air dry hide powder was introduced; into the second, 4 grams; the third, 8 grams; the fourth, 12 grams; and the fifth, 20 grams. They were placed in the shaker and shaken for six hours, then divided into three sets, each containing a determination with 2, 4, 8, 12, and 20 grams of hide powder. The first set was handled as in an official determination—squeezed through a cloth, kaolin added, filtered, 100 cc. pipetted, evaporated, dried and weighed

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and the amount of residue multiplied by 2 to give the total amount of soluble matter in 200 cc. The amounts obtained were deducted from the total solids in 200 cc. of the original solution and the differences obtained called the amount of tanning matter absorbed. The determinations in this set only differ from determinations by the Official Method in the use of air dry hide powder in place of wet, chromed powder and a period of shaking of six hours instead of ten minutes. Moreover, it has been claimed that the principle fault in the Official Method is due to measuring the concentration of that portion of the solution which constitutes the external phase and calculating this as the concentration of the entire solution, the error being due to a lesser concentration in the external phase in the presence of such non-tannins as are represented by gallic acid, and this difference is greatly augmented by an increase in the amount of hide powder and hence the internal phase. So therefore if we let this set of determinations represent the Official Method we at least have its greatest source of error included. The second and third set were washed fifteen and twenty times respectively as prescribed by the authors of this method. The original detannized solution and consecutive washings of each determination were collected in 2 liter volumetric flasks until washing was completed. Each flask was made up to volume and filtered clear with the aid of kaolin and 500 cc. collected in a volumetric flask for evaporation. The evaporation of each of the solutions from every determination was carried out in a single dish. The dishes were refilled from their respective flasks as evaporation proceeded. The combined residues of each determination were deducted from the total solids in 200 cc. of the original solution and the differences called the amounts of tanning matter absorbed under these specific conditions. A blank determination was run on the hide powder and each residue was corrected for the small amount of soluble matter given by it which was largely inorganic. The results of this series of experiments is given in Table 1. In Figure 1 the amounts of tanning matter absorbed as per cent of the extract is plotted.

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TABLE I.

Showing amounts of tanning matter absorbed from 200 cc. of a solution of liquid chestnut extract (12 grams per liter) with varying amounts of hide powder, before and after washing.

	Hide powder added Grams	T. S. in original solution Grams	S. S. in solution after Grams	Solids absorbed Grams	Per cent of extract absorbed
Before washing	2	1.225	0.5164	0,7086	29 50
	4	1.225	0.4300	0.7950	33.13
	8	1.225	0.3752	0.8498	35.41
	12	1.225	0.3480	0.8770	36.54
	20	1.225	0.3196	0.9054	37.72
After washing 15 times	2	1.225	0.6396	0.5854	24.39
	4	1.225	0.5433	0.6817	28.40
	8	1.225	0.4966	0.7284	30.35
	12	1.225	0 4534	0 7716	32.15
	20	1.225	0.4408	0 7842	32.68
After washing 20 times	2	1.225	0 6928	0.5322	22.18
	4	1.225	0.5913	0.6337	26.40
	8	1.225	0.5546	0.6704	27.93
	12	1.225	0 5110	0.7140	29.75
	20	1.225	0.5214	0.7036	29.32

ANALYSIS BY OFFICIAL METHOD

T. S.	51.02	N. T.	15.18
S. S.	48.75	T.	33.57
Ins.	2.27	T. S.-N. T.	35.84

It is surprising to note that the three curves follow the same general direction and are essentially the same. The upper curve which represents the Official Method is practically equidistant at the points determined from the corresponding points in either of the two curves obtained after washing. The point that shows the greatest deviation is that obtained for 20 grams of hide powder after washing 20 times and since this was the least tanned powder of any, it is safe to assume that this difference is due to soluble hide substance. In this connection it should be mentioned that traces of nitrogen were detected in all of the solutions but since the quantities were so small and the results obtained varied so erratically it was deemed better not to attempt to correct the residues for soluble hide substance.

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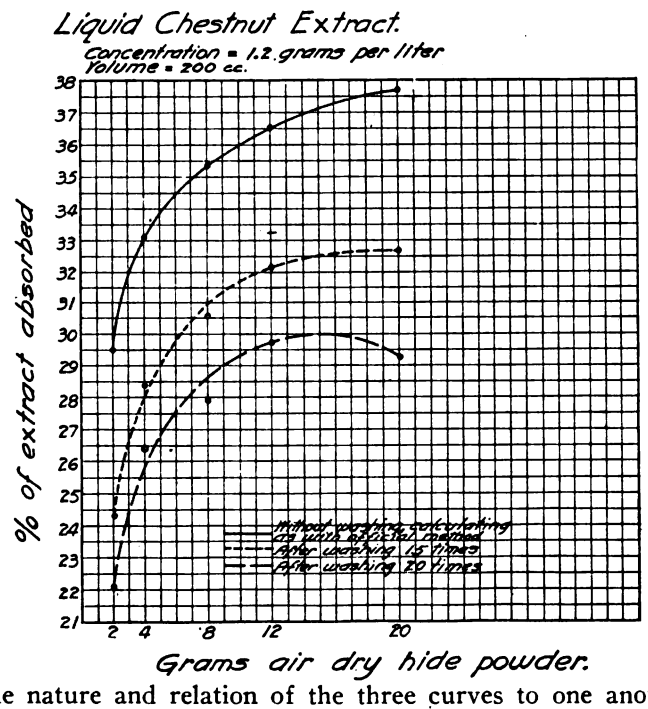
FIGURE I

Showing percent. of extract absorbed with varying amounts of hide powder, volume and concentration constant.



The nature and relation of the three curves to one another do not substantiate in any way, the assumption that the increased absorption obtained with increasing amounts of hide powder other conditions remaining the same, when operating as prescribed by the Official Method, is due to an increased absorption of non-tannins. If this assumption were correct together with the other claims made by Wilson and Kern then after thorough washing of the hide powder we should have a straight horizontal line. As it is we see that the middle curve is consistently lower than the upper by from 4.5 to 5 per cent while the lower curve is consistently lower than the middle one by from 2 to 2.5 per cent which means that an amount of material is removed by washing with a given amount of water that is practically constant for each determination and seems to point strongly to the partial removal of tannin by washing.

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In Table 1a and Figure 1a is given a similar set of results with solid quebracho extract.

TABLE Ia.

Showing amounts of tanning matter absorbed from 200 cc. of a solution of ordinary, solid quebracho extract (6 grams per liter) with varying amounts of hide powder, before and after washing.

	Hide powder added Grams	T. S. in original solution Grams	S. S. in solution after Grams	Solids absorbed Grams	Per cent of extract absorbed
Before washing	2	0.9926	0.1724	0.8202	68.35
	4	0.9926	0.0866	0.9060	75.50
	8	0.9926	0.0524	0.9402	78.35
	12	0.9926	0.0184	0.9742	81.18
	20	0.9926	0.1648	0.8278	68.98
After washing 15 times	2	0.9926	0.3808	0.6118	50.98
	4	0.9926	0.2432	0.7494	62.45
	8	0.9926	0.1856	0.8070	67.25
	12	0.9926	0 1488	0.8438	70.32
	20	0.9926	0.2472	0.7454	62.12
After washing 20 times	2	0.9926	0.4598	0.5328	44.40
	4	0.9926	0.3056	0.6870	57.25
	8	0.9926	0.2454	0.7472	62.27
	12	0.9926	0.2080	0.7846	65.38
	20	0.9926	0.3260	0.6666	55.55

ANALYSIS BY OFFICIAL METHOD

T. S.	82.72	N. T.	5.07
S. S.	73.83	T.	68.76
Ins.	8.89	T. S.-N. T.	77.65

It will be noted that the three curves in Figure 1a also follow the same general direction and are analogous. The difference between the points determined before and after washing do not coincide as in Figure 1 but this is probably influenced by the large amount of insolubles in this extract, and it is also probable that different results would be obtained with the use of wet powder in place of the air dry. The per cent of quebracho extract absorbed before washing and the amount held by the hide powder after washing 15 times differs by from 6.9 per cent to 17.4 per cent while difference for the chestnut extract

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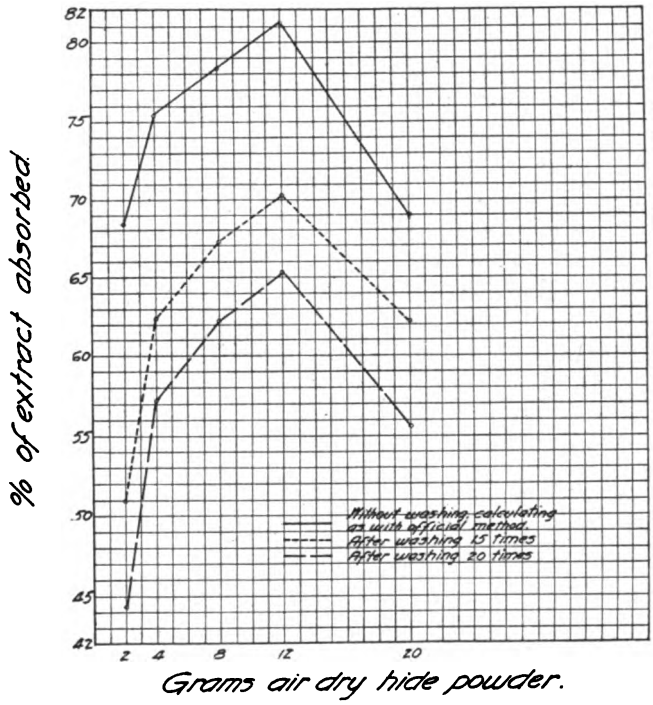
FIGURE Ia

Showing percent of extract absorbed with varying amounts of hide powder, volume and concentration constant.

Solid Quebracho Extract

Concentration = 6 grams per liter.
Volume = 200 C.C.



is from 4.4 per cent to 5.11. This indicates that under these conditions more material is removed in washing the quebracho tanned powder than in washing the chestnut tanned powder with the same quantity of water and if all of the claims were true that the authors make for this method there should be a greater percentage error in an official tannin determination on quebracho than on chestnut while the reverse is claimed to be the case.

Another series of determinations was carried out as described above, using liquid chestnut extract, by keeping the volume of the solutions and the amount of hide powder constant and varying the concentration. The results of the series is given in Table 11 anl plotted in Figure 11.

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TABLE II.

Showing amounts of tanning matter absorbed from 200 cc. of a solution of liquid chestnut extract of varying concentrations with 12 grams of air dry hide powder, before and after washing.

	Grams of extract per 100 cc.	T. S. in original solution Grams	S. S. in solution after Grams	Solids absorbed Grams	Per cent of extract absorbed
Before washing	0.72	0.7347	0.2108	0.5239	36.38
	0.90	0.9184	0.2634	0.6550	36.39
	1.20	1.2250	0.3480	0.8770	36.54
	1.44	1.4694	0.4224	1.0470	36.35
	2.40	2.4500	0.7472	1.7028	35.46
	3.60	3.6750	1.2106	2.4644	34.23
After washing 15 times	0.72	0.7347	0.2604	0.4743	32.93
	0.90	0.9184	0.3080	0.6104	33.91
	1.20	1.2250	0.4112	0.8138	33.91
	1.44	1.4694	0.5202	0.9492	32.96
	2.40	2.4500	0.9558	1.4942	31.13
	3.60	3.6750	1.5570	2.1180	29.42
After washing 20 times	0.72	0.7347	0.2976	0 4371	30.35
	0 90	0.9184	0.3480	0.5704	31.69
	1.20	1.2250	0.4688	0.7562	31.51
	1.44	1.4694	0.5778	0.8916	30.96
	2.40	2.4500	1.0202	1.4298	29.79
	3.60	3.6750	1.6608	2.0142	27.98

It will be seen that here also the three curves have the same general direction and it is interesting to note that there is a greater difference between the curves representing the Official Method and that obtained by washing the tanned hide powder 15 times when using a solution containing 3.6 grams of extract per 100 cc. than when using a solution containing 0.72 grams per 100 cc. The greatest absorption of non-tannin should occur at the weakest concentration in which case the percentage removed by washing a powder tanned with a solution of 0.7 should be greater than that with 3.6 grams. Although this relation exists after washing 15 times the differences at these two points are the same after washing 20 times, but at the dilution of 0.72 grams per 100 cc. the hide powder is relatively little tanned and the chances of soluble hide substance in the residue in slightly larger amounts is enhanced.

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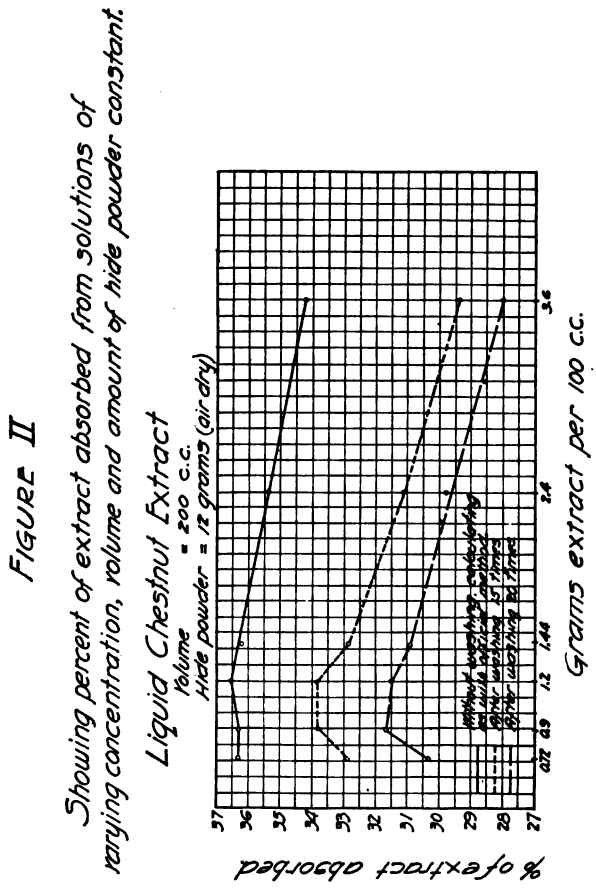

A final series of experiments was made with chestnut extract, using a constant amount of 7.2 grams of extract and 12 grams of hide powder at various dilutions. A solution of 36 grams of the liquid extract per liter was prepared and 200 cc. of this solution used for each determination and enough water added by means of a pipette to give the dilution desired. Otherwise the operation was the same as described for the preceeding experiments. The results of this series of experiments are given in Table III and plotted in Figure III.

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TABLE III.

Showing amounts of tanning matter absorbed from 7.2 grams liquid chestnut extract at different dilutions by 12 grams of hide powder, before and after washing.

	Volume, cc.	T. S. in original solution Grams	S. S. in solution after Grams	Solids absorbed Grams	Per cent of extract absorbed
Before washing	200	3.675	1.2106	2.4644	34.23
	300	3.675	1.2329	2.4421	33.92
	400	3.675	1.2906	2.3844	33.12
	500	3.675	1.3103	2.3646	32.84
	600	3.675	1.3280	2.3470	32.60
	800	3.675	1.3594	2.3156	32.16
	6000	3.675	1.7978	1.8772	26.07
After washing 15 times	200	3.675	1.5570	2.1180	29.42
	300	3.675	1.5170	2.1580	29.97
	400	3.675	1.5022	2.1728	30.18
	500	3.675	1.5130	2.1620	30.03
	600	3.675	1.4762	2.1988	30.54
	800	3.675	1.5130	2.1620	30.03
	6000	3.675	1.9275	1.7475	24.27
After washing 20 times	200	3.675	1.6608	2.0142	27.98
	300	3.675	1.6026	2.0724	28.78
	400	3.675	1.6094	2.0656	28.69
	500	3.675	1.6122	2.0628	28.65
	600	3.675	1.6042	2.0708	28.76
	800	3.675	1.6450	2.0300	28.20
	6000	3.675	2.0581	1.6169	22.46

Here also we see that the curves plotted for the per cent of extract absorbed by the hide powder before and after washing bear the same relation to each other as noted previously for results under other conditions. We see that with increase in volume, the amount of tanning material and hide powder remaining the same, there is a decrease in the amount of tanning matter absorbed by the hide. In going from the greatest dilution to the least it is seen that the two curves obtained for the washed hide powder depart from the general direction of the curve for the unwashed hide powder at 600 cc. This drop of the two lower curves is evidently due to an increase in insolubles in the stronger liquors, which become greater with increasing concentration and which

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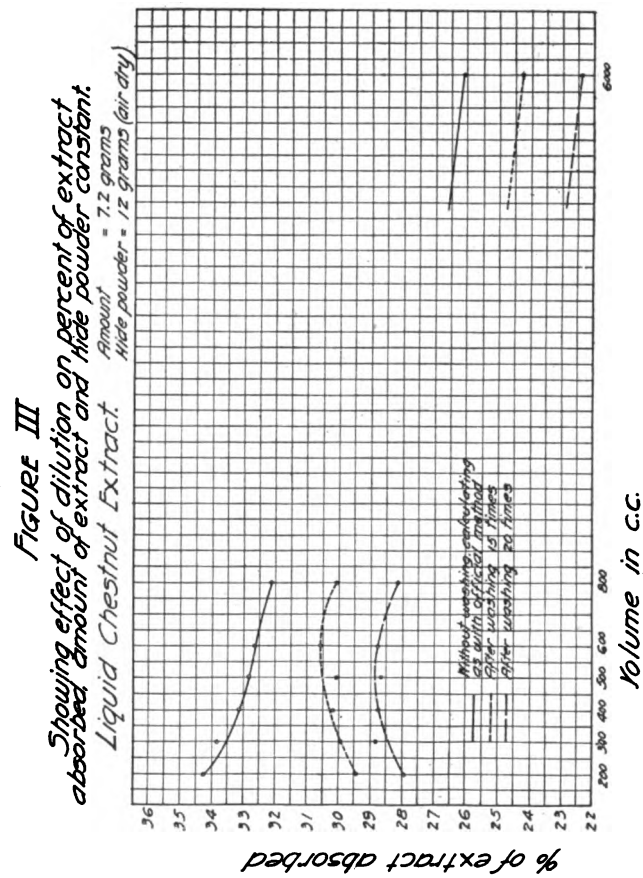
are absorbed by hide powder but apparently are partially washed out again without much difficulty. It is curious to note that the point at which this break comes is at the concentration of 7.2 grams of the extract in 600 cc. of water which gives about 0.4 grams tannin per 100 or the concentration prescribed by the Official Method.



It is seen from the preceding series of experiments that three factors influence the absorption of tannin by hide powder, namely, amount of hide powder, concentration of tannin and volume of solution, and that the affects produced are as pronounced after

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washing as they are before. Besides these factors, absorption is also probably affected by many others, such as, temperature, time of shaking, moisture content, degree of subdivision and acidity of the hide powder, the acidity of the solution and the characteristics of the tanning material, its solubility, power to associate, etc. The first three influences have long been recognized as well as some of the others mentioned, hence the limitations in the Official Method as to volume and cencentration of solution, amount and moisture content of hide powder, and time of shaking when a maximum absorption is obtained at least for the more common tanning materials.

It is likely that tannin in very dilute solution is but little better, if any, as a tanning substance than gallic acid, in fact it is probable that the only difference is the power of association which tannin possesses in a much greater degree than gallic or similar acids. This power of tannin to form molecular aggregates is in all probability different for the tannins of the different tanning materials which difference is not only due to the inherent nature of the various tannins but to other substances which co-exist with them and which are classed under non-tannins. We know that by increasing the strength of the solution of a given tanning material we increase the amount of insolubles up to a maximum after which they decrease again to a minimum which is obtained in a liquid extract. In speaking of insolubles here, references is to those which are formed from soluble material and which are not truly insoluble. Thus we have a minimum amount of insolubles formed at the lowest concentrations which increase to a maximum at an intermediate concentration after which it falls again to a minimum in a very concentrated solution. There must be a definite relation between the amount of material in solution, whether colloidal or molecular, and the amount of insolubles precipitated at equilibrium. This relation is evidently different for different materials as is evidenced by the fact that the insolubles are greater in a solution of quebracho extract than in a solution of chestnut of the same concentration and the increase is greater in the former than in the latter for small increases in concentration. It is evident that a similar relation exists between the amount of tannin in molecular solution and that in colloidal solution. This brings us to the conclusion that in a

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solution of tanning material we have tannin in all degrees of dispersion, varying from a molecular dispersion to one of suspension dimensions, and it is evident that the proportion of the least dispersed to the greatest depends upon the concentration. That tannin exists in true solution is proven by the fact that a portion of the tannin from a given solution will dialyse, in fact it is possible that tannin may even exist in ionic solution as is evidenced by a reported slight hydrion concentration.

The difference in the relation of the lesser dispersed to the greater dispersed particles between the different tanning materials must be due to a difference in the degree of association, characteristic of the various tannins or influenced by non-tannins, and can be roughly estimated by the solubility of the various materials The recognition of this property of the tannins will undoubtedly explain much in practice. Thus if we accept the solubility of various tanning materials as a rough criterion, judging of this from experience, and place them in the order of increasing solubility we have quebracho < hemlock < chestnut < oak < sumac, which is the reverse order to their weight giving properties in tanning but in the same order as would be obtained for rapidity of tanning which is dependent on the rapidity of penetration or diffusion, and the rate of diffusion for a given material is a function of the degree of dispersion. As is well known, spruce extract (sulphite-cellulose) is extremely soluble in water and penetrates hide very rapidly. If a piece of skin is tanned in a weak solution of spruce (of the same tannin concentration as will give a full piece of leather with a chestnut extract) and then washed, it will dry out almost like raw hide, with the exception of being discolored. Nevertheless there is a certain amount of the constituents of this extract that are fixed by the hide which cannot be removed by washing. The skin has been converted into leather but is extremely lightly tanned. It is my opinion that this is due to the fact that the tanning substance contained in this extract is not capable of associating to any great degree if at all. I believe that if a solution of such material is treated with successive portions of hide, each piece washed free of uncombined matter and the washings recovered and used again until all of the tanning matter has combined with the hide that will, it will be found that the amount capable

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of combining with hide will slightly exceed the result obtained by the Official Method. In other words I believe that the error in the Official Method lies in giving a result that is lower than the true tannin content.

A freshly prepared, dilute solution of tanning material may contain the tannin primarily in molecular solution but on standing or subjecting to prolonged heating (for both ageing and prolonged heating enhance the property of association in most dispersed systems) the tannin may exist largely in the colloid state. This will no doubt explain why as much, if not more, combined tannin is found in leather that has been tanned with weaker solutions in a greater time period. To obtain the same results with less time we have to increase the concentration of tannin which causes an increase of particles in the colloid state. Increasing the concentration of the liquors up to a certain point is attended by an increase of concentration in the internal solution and a large increase in insolubles in the external solution. The latter is removed eventually from the process as sludge and thereby makes this method of tanning more costly in tanning material.

From all this it is evident that the true *tanning value* of a tanning material is dependent on many influences and varies for the condition of solution and the conditions under which it is brough into contact with hide but it is obvious that the true *tannin value* of the same tanning material must be constant for all conditions. There cannot be a definite relation between the two values so that one can be estimated from the other for all vegetable tanning materials unless the characteristics of the several tannins and the optimum state for tanning with each of the materials are known. The case is somewhat analogous to that of a solution of bichromate and one of similar chrome content that has been rendered sufficiently basic for tanning. An analysis of these two solutions show that the chromic oxide content is the same, yet the former has no tanning action while the latter has. The potential tanning power of the one is as great as the other but the actual tanning power is entirely different. In other words, analysis shows us that the tannin content of these two solutions are the same but practice shows that the tanning values are two extremes. The one only differs from the other in being in the proper state for tanning. Perhaps a

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better example and analogy would have been presented by chrome alum where we have a slight tanning effect with the solution of pure material.

While all that has been said above seems to be confirmed by the experiments presented in this paper and by practice it is recognized that the data are too few for a general theory. What has been said is more to give some of the essential features of a working hypothesis with which it is hoped that this work can be continued, so as to eventually fix the validity of the Official Method of tannin analysis and also gain some idea of the mechanism of tanning with vegetable materials.

It has been demonstrated that the Wilson and Kern method of tannin analysis is based on a series of false assumptions. This method neither gives the true tanning value of tanning materials nor the true tannin content. Although the absolute accuracy of the Official Method is still in doubt the method embodies correct scientific principles for obtaining the maximum fixation of tannin and all indications seem to point to the fact that the error in this method is not as great as commonly supposed. Therefore there is no reason to look askance at the results obtained by it until its accuracy is correctly determined.

In conclusion the author wishes to acknowledge his indebtedness to Mr. W. K. Alsop, for inspirations obtained in the course of frequent discussions of the subject, for criticisms and for making it possible to carry out the experimental work.

ELK TANNING COMPANY LABORATORY
Ridgway, Pa.

TANNING MATERIALS IN THE FAR EAST.*

By Lloyd Balderston

In Japan and China the per capita use of leather is small. In Japan the standard footwear is a wooden clog, held on by strings of cloth or leather. For a long time the principal use of shoes was for the army, but their use among civilians, especially men and boys, is rapidly increasing. Even yet the quantity of shoes

* Presented at the Eighteenth Annual Meeting at Atlantic City, June 10, 1921.

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used is small compared with Western peoples. Harness leather also is in small demand because horses are used but little in farming in most parts of Japan, and in cities much of the tranportation is by man-drawn vehicles.

In China a large part of the population habitually go barefoot. The footgear of those who can afford it is a low slipper which may be of leather, but is oftener made entirely of fabric. Leather plays little part in the extremely primitive harness used on draft animals in China, so that the per capita consumption of leather is even less than in Japan.

As to raw material for leather making, China produces far more than Japan, as Japan has but few domestic animals. As in known, China exports most of her hides and skins, while Japan tans all she produces and imports from all over the world, China and Manchuria furnish most of the Japanese imports of hides and skins.

Of the leather used in China, a large part is imported, and it is often difficult to learn anything about the sources or methods of manufacture of the leather one sees exposed for sale. The merchant professes to know nothing about it. He classifies his stock as red and white. Red leather is made in the Singapore region by Chinese with mangrove bark. It is thin and poor. White leather includes all other sorts; vegetable tannage from the west, white by comparison with the dark red mangrove leather, and native products made with alum, glauber salt or smoke.

China has no forest reserve except in the mountains of the extreme west and north. Wood from these sources comes down the great rivers to supply the modest demands of Canton and other cities for lumber and firewood. The junks carry wood not only in the hold and on the deck, but slung over the sides in festoons. Tanbark is, however, an unknown article in Chinese markets. A few myrobalans are said to be grown in northern Kwantung, near the coast, but they seldom or never are seen elsewhere. The standard methods of leather-making in China are smoke tannage and various mineral tannages. I have seen a number of samples of smoke tanned leather. It is very thin and light-colored rather stiff and quite tough. It must be absurdly cheap. A passenger on the steamer had a deck chair whose combined seat and back were made of this leather; a piece

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some 4 feet by 16 inches. There was also a sort of pillow involving perhaps 2 square feet more. The frame was substantially built of hard wood. It was made at one of the coast towns south of Shanghai. The source of the leather was somewhere inland; it had come down river. The chair cost less than $2 American money.

A group of Japanese officers have studied smoke tannage, and written a description with illustrations. One of the instructors at Hokkaido University has promised to translate this for me, so I hope it may appear in print. I know of no adequate description in English.

Some of the leathers on sale in Canton are really white, and seem to be tanned by some mineral process. I have examined white sheep leather from Hankow, which was at least partly tanned with glauber salt. Many of these white sheepskins are split, the grain only being taken off and used to cover wooden boxes to serve as suitcases. I saw several of these boxes on the steamer. They are very neatly built, with brass lock, handle and hinges. The rest of the sheepskin is a by-product. Some of these undergrain splits find their way from Hankow to Japan.

Another method of which I heard is practiced in Manchuria and is spoken of as milk tannage. The material actually used is a fermentation product of milk called yogurt. I suppose the process is really a sort of fat tannage. I have a pretty good description of this method which has been translated and will be offered for publication in the JOURNAL.

Besides these various indigenous methods, China has a few modern tanneries run on Western lines. One of these is at Shanghai, owned by the Japan Hide and Leather Company. One at Canton, on the south side of the river, I had the good fortune to see. Mr. Chu, assistant professor of Chemistry at Canton Christian College, took me to see it. This small tannery makes only black upper leather by the one-bath chrome process. The manager is Mr. Ching, a graduate of the University of California and of the tanning courses at Pratt Institute.

Most of the processes are carried out with modern machinery driven by a Diesel engine built in China. The splitting is done by hand, and I consider myself very fortunate to have witnessed

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this process. The workmen sits in front of a low level table, holds the hide over the edge with one hand and with the other pushes a knife shaped like a short thin chisel about 2 inches wide. The resulting split is very accurate in thickness and has a smooth surface.

The chrome for tan-liquors at this tannery is obtained from America, being in the form of a copyright named ready prepared material. Mr. Ching knew of no Chinese source of chrome in usable shape.

Very few indigenous tanning materials are now being utilized in Japan, nearly all of the vegetable material coming from two species of oak. Besides these there are two things which are really tanning materials but are not used in making leather. One is the root of the beach rose, *Rosa rugosa*. The bark of this root has 24 per cent tannin (dry basis). It used to be employed in tanning fish nets, but this is now done with oak extract, and the present use of the rose root is as a mordant in silk dyeing. Leather made with this tannin is very dark colored.

The other material alluded to is the juice of a small green persimmon, sold in liquid form under the name "shibu." The adjective describing the taste of a green persimmon is "shibui." This juice is used in preparing a sort of waterproof paper and in staining floors.

In Hokkaido, the northernmost district of Japan, several factories have been in operation making oak extract. Oak bark is also shipped in sacks and bundles to the tanneries of Tokyo and Osaka. One of the largest of the extract factories, owned by the Japan Hide and Leather Company, was described in This Journal 13, 305 (1918). I am told that this plant will soon close down because of lack of materials, as the supply of oak bark is rapidly falling off.

Many kinds of imported tanning materials are used in Japan. Wattle bark and quebracho extract are probably most important, but some California oak is used, and a considerable quantity of myrobalans from India.

It seemed to me that oaks were probably not the only timber trees of northern Japan whose bark contained tannin in commercially available quantity. I therefore examined the bark of some 25 species and the wood of 8. Some of these belong to genera

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not represented here, none of which has important amounts of tannin. Two are large alders. I have heard of an alder whose bark is worth peeling, but neither of those I examined is worth anything. Two are magnolias, also negligible as to tannin; one has 16 per cent non-tannins. One is an ironwood, *Carpinus cordata,* having nearly 6 per cent[1] tannin in its bark. The Japanese walnut, *Juglans sieboldiana,* has a heavy bark with about 6 per cent tannin.

I examined two willows. *Salix caprea* is a good-sized tree. the bark of which has more than 8 per cent of a very good tannin. The other, *Salix purpurea,* is used in basket making, and the bark is stripped off and destroyed. This bark has 7.5 per cent of good tannin and 23 per cent non-tannins. When used alone it penetrates slowly but makes very nice leather.

The Japanese chestnut, *Castanea pubinervis,* does not seem to grow so large as our chestnut, which it closely resembles in the appearance of wood and bark. The leaf is much smaller than that of our tree, and the fruit a good deal larger. The bark has about 6 per cent tannin and 7 per cent non-tannins; the wood nearly 7 per cent tannin with 4 per cent non-tannins. There is no considerable supply of chestnut available, so it is not likely to become a source of commercial tannin.

There are three oaks native to Hokkaido. The smallest of these, *Quercus glandulifera,* is poor in tannin, only about 4 per cent being in the bark and less than 2 per cent in the wood. The second in size, *Q. dentata,* is most important as a tannin source, averaging about 11 per cent tannin in the bark, with 10.5 per cent non-tannins. The wood has about 7 per cent of each *Q. grosseserrata* has about 9.2 per cent of each in the bark, and one fourth as much in the wood. In both these larger oaks the outer bark has less than half as much tannin as the inner.

Quercus grosseserrata is called water- oak. It is a large tree, much resembling in all respects our chestnut oak, *Q. prinus.* The wood, which is perhaps a little lighter in color than that of the chestnut oak, is much valued for cabinet work and other purposes appropriate to high grade oak wood. The specific name of *Q. dentata* refers to the rather large rounded teeth of

[1] All of these figures are based on water free material.

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the leaf. The wood is rather harder and darker than the other, and the medullary rays are strongly marked. The tannin of these two oaks is indistinguishable in color and quality, quite as good in every respect, I think, as our chestnut oak.

Japan has many coniferous trees. Only those were examined which grow in Hokkaido and are commercially important on account of their wood. The yew, *Taxus cuspidata*, is very similar to the European yew, *T. baccata*. Its wood is very valuable close-grained, hard, dark red and fragrant. In old times in Europe yew wood was used for bows and the aborigines of northern Japan made their bows of it also. It is now used for cabinet work and fine cooperage, but probably the most important use is for lead-pencils. It is harder than our red cedar but otherwise much like it. The chips furnish a valuable dye. The bark of the yew is thin and stringy, containing about 9.5 per cent of a rather dark colored tannin and nearly 16 per cent non-tannins.

There are two very similar larches, the bark of one of which, *Larix dahurica*, contains about 8.5 per cent tannin and 6 per cent non-tannins. This tree has been extensively planted in Hokkaido, and its bark may become an important source of tannin, whose quality much resembles our hemlock, though it is not so red.

Of true pines, only two seem to be commercially important, being extensively used in the south for firewood. These are *Pinus densiflora* and *P. thunbergii*, called respectively the red and black pine, from the prevailing color of the bark. They are the pine trees so familiar in Japanese poetry and art.. They both tend to grow in grotesquely irregular shapes. They are extensively used in parks and gardens, and the gardener encourages them to form lopsided and otherwise bizarre tops. As a tannin source neither is important. The tannin of both is dark colored, and amounts to about 6 per cent in each case, with larger percentage of non-tannins. Both have rather heavy insolubles, the black pine exceeding 7 per cent.

Two very notable species of conifers of high importance as timber trees, were not examined because they do not grow in the north and I did not have opportunity to procure samples of the bark. The two are the Japanese cedar, *Cryptomeria*, and the "Hinoki," a species of *Chamaecyparis* which may be called the Japanese arbor vitae. The genus *Cryptomeria* is peculiar to

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Japan, and there is but the one species. These are both noble trees, whose wood is very valuable. That of the hinoki resembles Canadian white cedar. The bark of this tree is used for roofing. It is dry and fibrous, and I should not expect to find much tannin in it. The Cryptomeria is specially celebrated for its beauty. The forests which surrounded the temples and tombs at Nikko, and the great avenue lined on both sides with these trees for many miles, leading from Nikko toward Tokyo, are among the most worth while sights of Japan.

By far the most important conifers of northern Japan are three spruces whose wood is not easily distinguishable. One of these called in Japanese "Todomatsu," is a balsam spruce. The general appearance of the heavy bark of the mature tree is almost white. There are two very similar species, but I met with only one, *Abies sachalinensis,* whose bark contains from 7 to 10 per cent of a beautiful resin much resembling Canada balsam. The refractive index at 18 degrees C. is 1.504, somewhat less than that of Canada balsam. The tannin content of the bark is 2 per cent, non-tannins nearly 13 per cent.

The other two spruces are *Picea yezoensis* and *Picea glehni* Those both grow to great size. The former called "Yezomatsu," has a heavy, light colored bark, with a curious habit of coming off in irregular somewhat lens-shaped plates, up to 1½ inches in diameter and ⅜ of an inch thick. On large trees the whole thickness of the bark exceeds one inch. It contains about 9 per cent of a dark-colored tannin and as much non-tannin. I judge this material to be fairly comparable to the "fichte," often spoken of as pine bark, so much used in sole leather tannage in central Europe.

The third spruce, *Picea glehni,* prefers moist localities. It is called red yezomatsu because of the general appearance of the bark,which is much thinner than the last, not much exceeding half inch even on large trees. It splits off in somewhat similar fashion, but in smaller pieces. With the possible exception of *Pinus halepensis,* this is richer in tannin than any coniferous bark of which I have any knowlege. An average of four analyses of the whole bark gives 19.2 per cent tannin and 12.4 per cent non-tannins. This material is even more remarkable for color and quality than for high percentage, giving a leather both

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lighter in color and brighter than either of the oaks, and quite equal in strength and "feel" to leather tanned with wattle bark.

The wood of these three trees is much like our white spruce in appearance. The grain is not quite so strongly marked, and the wood is neither so hard nor so strong as our spruce. It is a little harder than our white pine, but works much like that wood. The three kinds are used very extensively and generally without discrimination for lumber and for paper making. The bark is in all cases wasted, the fact that two of the kinds are valuable as tanning material having been unknown. The logs which are used for paper pulp are peeled in the woods and the bark simply left on the ground. I estimate from the government figures of timber consumption that the annual waste of coniferous tannins approaches $100,000 in value. There is also a heavy waste of oak bark, as winter-cut oak wood is extensively used for fuel and the bark left on. No figures on this are available.

The following table gives more complete figures on the analyses of some of the materials mentioned: percentage on dry basis.

Materials	Total solids	Soluble solids	Insolubles	Non-tannins	Tannin
Quercus dentata, bark	26.7	21.8	4.9	10.6	11.2
Quercus dentata, wood	15.9	14.1	1.8	7.2	6.9
Quercus grosseserrata, bark	20.0	18.5	1.5	9.3	9.2
Quercus grosseserrata, wood	5.0	4.8	0.2	2.1	2.7
Castanea pubinervis, bark	13.8	13.1	0.6	7.1	6.0
Castanea pubinervis, wood	11.0	10.6	0.4	3.9	6.7
Salix caprea, bark	19.0	16.6	2.4	8.4	8.2
Salix purpurea, bark	32.7	30.6	2.1	23.1	7.5
Pinus densiflora, bark	18.2	15.1	3.1	8.7	6.4
Pinus thunbergii, bark	18.9	12.6	7.3	6.8	5.8
Taxus cuspidata, bark	27.9	25.3	2.6	15.7	9.6
Larix dahurica, bark	16.1	14.5	1.6	6.1	8.4
Picea yezoensis, bark	20.6	17.8	2.8	8.8	9.0
Picea glehni, bark	37.1	31.6	5.5	12.4	19.2

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BOOK NOTICES.

THE ACTIVATED SLUDGE PROCESS OF SEWAGE TREATMENT. By J. Edward Porter. Publishers, General Filtration Co., Inc., Rochester, N. Y. Price, $1.00 plus first class postage of $.16.

This book of 117 pages is a complete abstract bibliography of all that has appeared in literature on this process of sewage treatment, arranged in chronological order from the beginning (1912) to the end of 1920. Besides a comprehensive abstract of each article, complete references are given to the original. The accumulation of all this data in book form should be of inestimable value to all who are interested in the subject and it is extremely possible that tanners will be compelled to show more interest in this subject in the future. It is interesting to note that the author records five private experimental plants in this country operating on tannery sewage and one plant that is evidently beyond experimental stages, all of which are using the activated sludge process.

DIE LOHGERBEREI ODER DIE FABRIKATION DES LOHGAREN LEDERS (Vegetable Tannage or the Manufacture of Vegetable Tanned Leather). By Ferdinand Weiner. Third, enlarged and improved edition. 518 pages with 76 figures. A. Hartleben's Verlag, Vienna and Leipzig. Price 14.4 marks.

In the preface the author states that this book was prepared to inform the practical tanner of the progress in his field of endeavor and to serve as a text book for the beginner. The fact that it now appears in the third edition must give some idea of the popularity of the book and the demand for it. Although this work contains many statements that do not conform to fact such should not seriously detract from the value of the book, as it contains much of interest even for one of wide experience. The treatise is very thorough and most subjects are elaborately treated in detail with explanations of the cause and effect. The raw materials for vegetable tanning are discussed which is followed by a treatment of the methods of preparing hides for tanning. The old method of pit tannage is explained and also the various methods of drying, leaching and the preparation of tanning liquors, and rapid tannage. In lieu of the importance of machinery in tanning, the author devotes a great deal of space to a description of the various machines used. Chapters are devoted to the stuffing, bleaching and blacking of leather; leather specialties; the dyeing and enameling of leather; and the disposal of tannery wastes. Most of these subjects are necessarily briefly treated and can only be considered as summaries.

DIE WEISZGERBEREI, SAMISCHGERBEREI UND PERGAMENTFABRIKATION (Tawing, Chamois Tanning and the Manufacture of Parchment). By Ferdinand Weiner. Third edition, revised and enlarged by Viktor Mikuska. 351 pages with 24 figures. A. Hartleben's Verlag, Vienna and Leipzig. Price 24 marks.

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In revising this book, Prof. Viktor Miluska states that he has adhered to the original plan of the author which was to present this work as simply as possible so as to serve as a guide and instructor for the practical worker, and at the same time to bring the book up to date. The introductory portion of the book is devoted to a discussion of the structure and properties of animal hide; the author's views on the nature of the tanning process; the physical and chemical properties of vegetable tanning materials, of aluminum salts and the alums; fats used in tanning; the various hides used in tawing and chamois tanning; and the preservation and disinfection of hides and skins. Under the subject of tawing, to which more than half of the book is devoted, the various modes of tawing are described, also the various processes of unhairing, deliming, plumping and finishing. The section on chamois tanning consists of a description of oil tannages and includes a chapter on the various parchments. The book is concluded with a brief section on the dyeing of tawed and chamois leathers.

ABSTRACTS

"Tizera," A New Tanning Wood. By W. EITNER, *Hide & Leather*, March 26, 1921, 33 "Tizera wood is derived from an *anacardiaceae*, probably *Pistachia lenticus* or *Pistazia nera*. The tree grows in the Mediterranean countries, especially in Sicily, often in North Africa and also in Central America. The reddish heart wood is surrounded by a yellowish sap wood which forms about 10 per cent of the mass. Well dried wood in its original condition gave:—

Water	9.90
Tanning Matter	30.62
Non-tannin Matter	2.27

The tannin from tizera-wood compares very favorably with that from quebracho, it penetrates easily and tans through quickly although it does not give quite as good yields as quebracho. It is less astringent than quebracho and more soluble. The color of tizera tanned leather is pale pink similar to that produced by mimosa bark. It can be used in tanning to modify the color of other materials with good results. If the extract can be produced in sufficiently large quantity it can successfully be used to displace quebracho.

Pelt Dyeing. By O. BERTHOLD, *Deut. Farber-Ztg.* 56, 845 (1920); *C. A.*, 15, 774 (1921). After tanning the pelt which is to be dyed is prepared by maceration in a 1-3° Bé. sodium hydroxide solution, then washed in a large amount of 0.5 per cent sodium carbonate solution. In place of sodium hydroxide, milk of lime, sodium carbonate or ammonia of corresponding concentration may be used. The temperature should not be above 30°. The skins are then washed free of alkali, are made slightly acid with acetic or formic acid and again washed. Mordanting previous

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to dyeing yields faster colors. The following mordants are recommended, the amounts in each case to be added to 1 liter of water: (1) potassium bichromate 2 grams, tartaric acid 1, copper sulphate 0.25; (2) potassium bichromate 2, tartaric acid 1; (3) potassium bichromate 2, acetic acid 1-2 cc. 30 per cent; (4) copper sulphate 5, acetic acid 1-2 cc. 30 per cent; (5) ferrous sulphate 2/5, acetic acid ½ cc. 30 per cent; iron liquor 20-50 gr. 30° Bé. These mordants may be used singly or in mixtures at temperature of 25-30°. For dyes ursols are recommended the dye being formed on the hair by the oxidizing action of hydrogen peroxide, the complete effect requiring 4-18 hours. A fine deep black on rabbits pelts is obtained, after the usual preparatory treatment, by mordanting with copper sulphate and acetic acid for 15 hours at 30° and thorough washing, then dyeing in a bath containing ursol D 6 grams, ursol DG 2 grams and 120 cc. hydrogen peroxide solution for 15 hours at 30-35°. The pelts are then thoroughly washed and placed in a fresh cold bath containing copper sulphate 0.5 gm. per liter for 2-3 hours, centrifuged without washing, and the leather coated with a solution containing sodium chloride 200 gms., glycerol 100 and egg yolk 40 per liter, when the pelts are dried, stretched and finished.

Chemical Reaction Affects Casein Glue. *Technical Note No. 138,* Forest Products Lab., U. S. Forest Service. Although casein glues are highly water-resistant, they ultimately decompose when exposed to a damp atmosphere for a long time. For many months studies have been under way at the Forest Products Laboratory to discover the cause of this decomposition.

The decomposition study is still far from complete, but the conclusion has been reached that the decomposition of ordinary alkaline casein glues is not due to the action of bacteria or molds. It appears to be due entirely to chemical action of the alkali in the glue. This conclusion is based upon the following observations:

"Increasing the amount of alkali in the glue increases the rate of decomposition when the glue is kept wet.

"Glues containing no sodium hydroxide, although deficient in some important respects, do not decompose as rapidly as similar glues containing sodium hydroxide.

"Cultures of molds and bacteria could not be obtained from decomposed alkaline glues.

"Some chemicals which have antiseptic properties are found to improve casein glue, but this improvement is due to their chemical action rather than to their toxic properties.

"Glues can be completely decomposed in a short time at temperatures above that at which bacteria can grow."

Further work is being directed toward the production of glues which will resist chemical decomposition and at the same time be impervious to the action of fungi and bacteria as well as moisture.

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The Biologic Significance of the Tannic Substances. By A. De Dominicis and R. Spataro, *Staz. sper. agrav. ital.* 52, 305 (1919); *C. A.*, 15, 874 (1921). Ten drops of 10 per cent solution added to 20 cc. 0.1 per cent albumin solution caused coagulation, merely opalescense in the presence of 6 drops of citric acid and had no effect in the presence of 6 drops of acetic or tartaric acid (all 10 per cent). Tannin is a very strong protoplasmic poison, coagulating albumin. It appears in the germination of seeds, which are initially free from it, and hence cannot be considered as a reserve material for either the sugar contained or for those compounds which, accumulating in the free state, would be harmful. Tannic substances may be considered as secondary products of exchange of materials but in this sense the esterification of the phenolcarboxylic acids forming their nucleus cannot be attributed to the same reason as the formation of other glucosides, namely the neutralizetion of the toxicity of products resulting from vegetable metabolism, for gallotannic acid is more toxic than gallic. Wood shows a much higher coefficient of absorption for tannin than for gallic acid, yet the more easy elimination of the tannic substances in the glucosidic state by the absorptive action of the cellulose of the wood cannot be the only reason for their formation. The principal reason is their ability to be oxidized more readily than the phenolcarboxylic acids from which they are derived. The tannin disappears by complete oxidation in fleshy fruits when the coagulating power of the tannin itself is no longer neutralized by the free organic acids which disappear with maturation. In other organs, however, an equilibrium is established between the tannin which is formed in or brought to the organ and that which is destroyed by combustion. In the bark, directly exposed to the atmosphere and to variations in external agents, this equilibrium is subject to displacements the most significant of which is caused by the increased oxidation brought about by rise in temperature which reaches its maximum during the hottest months of the summer. Tannic substances, therefore, in the glucosidic state, represent refuse material which the plant can easily destroy by the vital process of combustion.

Separation and Detection of Lactic Acid as Complex Sodium Ferric Lactate. By K. A. Hoffman, *Ber.* 53, 2224 (1920); *C. A.*, 15, 813 (1921). The salt is practically insoluble in water and is formed as a pale green precipitate by digesting a dilute solution of lactic acid with ferric chloride for some time. The iron is present in a complex anion. By shaking with water, a pale yellow suspensoid is obtained of neutral reaction. Dilute ammonium hydroxide solution attacks the precipitate exceedingly slowly and 15 per cent acetic acid has practically no effect on it. Stronger acids dissolve it and stronger bases decompose it, forming the hydroxide. To detect ordinary lactic acid with the aid of this salt, add a slight excess of ferric chloride, make distinctly alkaline with sodium carbonate and then add acetic acid until acid. Concentrate the solution on the water bath and after a few hours the precipitate will form even when only a little lactic acid is present.

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The Mangrove of Lower Congo. By R. LEMAITRE, *Bull. agr. du Congo Belge*, 10, 84 (1919); *C. A.* 15, 957 (1921). Analyses of the bark from various heights above the root gave from 9.56 to 19.30 per cent tannin on the dry bark. The ratio of tannin to non-tannin in extracts made varied from 0.4 to 1.3. The per cent moisture in the bark after 15 days drying in the shade ranged from 26.6 to 46.5.

Note on Some Tanning Materials of the Belgian Congo. Possibility of Their Utilization in the Manufacture of Dry Extracts. By E. NIHOUL, *Bull. agr. du Congo Belge*, 10, 89 (1919); *C A.*, 15, 957 (1921). Results of analysis of various materials were:

	Per cent tannin in total extract	Ratio of tannin to non-tannin	Per cent tannin in original dry matter
Terminalia catappa	82.73	5.0	28.3
Boembe	79.67	3.6	12.2
Albizzia Lebbeck	78.59	3.6	12.5
Bempanze	77.53	3.4	14.6
Bakalaka—*Carapa procera*	73.81	2.8	13.4
Ikingereke	70.66	2.4	15.8
Wenge	69.24	2.2	12.0
Sowoolo or Isasange	67.51	2.0	14.1

Finishes and Seasons for Leather. ANON., *Lea. Tr. Rev.* 54, 197 (1921). The primary object of a finish or season usually is to obtain a bright surface on the good. Other objects for applying finishes or seasons to leather differ for the different kinds of goods and may be for the purpose of providing a film that will take the friction produced by the mechanically propelled glass or steel roller; to fill up a porous grain and to cover certain minor defects; to give an artificial grain on splits; to "mat down" the fibers on the flesh side; and to give a dull finish to bright finished goods. The materials used for finishes and seasons are; (1) gelatines and glues, (2) albumens and albumenoids, (3) vegetable and animal waxes, (4) vegetable mucilages, (5) starches, (6) gums, (7) preparation of nitrated cellulose. Occasional additions include soaps, oils, spirit, alkalies, acids, glycerine, dyes and mineral salts.

Acid Unhairing. By R. H. MARRIOT, *J. S. L. T. C.*, 5, 2 (1921). Various pieces of hide and skin were unhaired by the aid of dilute acids with or without the addition of neutral salts, and the following results were arrived at:—(1) The depilatory action is not bacterial. (2) This mode of unhairing is not so effective as ordinary liming, the hair cannot be removed so easily. A section of the skin shows that sudoriferous and sebaceous glands are still present. (3) There is an action similar to that of bating. A skin well unhaired in ¼ per cent acetic acid, was, after tanning and finishing, but not bating, softer than a limed and

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bated skin. (4) The acid liquor appeared to contain unhydrolysed gelatin. (5) A ferment which produces alcohol was found to develop in the liquor. (6) Unhairing is probably due to the hydrolytic action of the acid on some prosthetic protein similar to mucin, the carbohydrate group being attacked by the ferment.

Examination of Roman Leather. By J. ATKIN and R. H. MARRIOT, *J. S. L. T. C.*, 5, 10 (1921). A fragment of Roman leather found during excavations on the site of a Roman fort at Slack near Huddersfield, England, was examined and results obtained as follows:—

	Calculated to air dry leather
Moisture	14.0
Hide Substance	47.0
Insoluble Ash	15.3
Water Solubles	2.5
Difference from 100 per cent	21.2

The difference from 100 per cent called combined tannin gives a degree of tannage of 45. The ash consists almost entirely of iron aluminum and silicon oxides apparently derived from the clay in which it was imbedded. The tannage is vegetable and the leather is in a remarkable state of preservation as indicated by photomicrographs of the grain and cross section.

The Use of the Microscope in Leather Manufacture. By A. SEYMOUR-JONES and F. L. SEYMOUR-JONES, *J. S. L. T. C.*, 5, 56 (1921). A brief review of microscopial research as applied to the problems of the leather industry that have already been accomplished and indications for lines of future work that is both needed and likely to prove fruitful.

The Soaking of Dried Indian Hides. *Lea. World*, 13, 317 (1921). Under-soaking will give harsh, pipey grain whilst over-soaking will give soft, flannely leather which breaks up and gives a characteristic loose grain. Hides which have been dried at too high a temperature would lose much valuable hide substance in the great length of time they would require to soak back in ordinary water and it is this loss of hide substance which causes the main defects in many of the dry hides tanned. It is therefore necessary to use chemicals in soaking to obtain the desired results in the shortest time and with a minimum loss of hide substance. Either alkalies or acids may be used. The alkalies most commonly used are caustic soda and sodium sulphide, the amounts recommended without fear of ill effects are 20 lbs. of caustic soda and 30 lbs. of sodium sulphide to 1,000 gals. of water. On the second day of soaking in such, some of the hides are ready for drumming. Hides which are not sufficiently soft should not be

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drummed because of the danger of broken grain. The hides are drummed in a dry drum for 20 minutes, when they are put back to soak in a fresh water containing 10 lbs. of caustic soda or 15 lbs. of sulphide. A day's soaking in this liquor should render the hides fully ready for liming.

The best and safest acid for soaking is formic although great care must be taken in its use. The usual method is to throw the hides in clean water for a day when they are opened out and put down in a solution of one tenth per cent of formic acid. They are drawn each day until soft and in condition for drumming, drummed 20 minutes and put back into the soak for at least a day before going to the limes. When formic acid is used for softening it is necessary to increase the amount of sulphide in the limes as formic acid slows up the liming.

The Manufacture of Heavy Upper Leathers. ANON., *Lea. World*, 13, 224 (1921). For black harness leather the ideal pelt is given by the bull, but for boot uppers and light harness, kips and cow hides are mainly used, and for inferior quality, dry hides. A good soaking is essential and can be accomplished either in pits or in latticed drums. The Tillson-Melbourne process is also recommended. Oniy dried hides need a "sharpened" soak. After soaking, the hides are put through the fleshing machine to free them from superfluous flesh so as to obtain a much more level liming. For liming, the use of mechanical means to hasten the process and save manual labor is recommended and the Tillson-Melbourne and the old revolving-lime system is discussed. After liming unhairing and fleshing the hides are surface delimed before bating. Hydrochloric acid (about 0.9 to 1.0 per cent of pelt weight of commercial acid) is satisfactory and should be done at a temperature of 85° F. in latticed drums. Instead of hydrochloric use can be made of boric or an organic acid of which lactic is the safest. Bating can be done either in pits or in a drum with the use of dung or artificial bates. After bating the goods are scudded. Prior to tanning it is recommended that the goods be hung in a 0.5 per cent solution of formaldehyde for four or five days or treated with a synthetic tannin to better prepare the pelt for strong liquors without "drawing" the grain and for a better absorption of tan. This preliminary treatment also increases the tensile strength enormously. The hides are then put through a series of six suspenders, the bottom one measuring 20° barkometer and the top one 50°, giving two to three days in each. When the hides have reached the last suspender they should be struck through or nearly so. They are then sent to the splitting machine and subsequently sorted and shaved. Then they are tanned in the drum, using a blend of sulphited quebracho and chestnut or oakwood extracts, to which has been added 5 per cent on the shaved weight of synthetic tannin extract. The whole mixture to measure about 60-65° barkometer. The hides are left in the drum for 48 to 72 hours, drumming only one hour in the morning and two in the afternoon. Or they may be drummed continuously for 12 hours, the temperature of the liquor should not exceed 40° C. After tannage all superfluous tan is washed

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cut, the goods sammed and stuffed lightly in the hot stuffing drum. They are then dried, sammed and struck out, oiled off on the grain, sammed again, set out by hand and finally dried out completely when they are ready for finishing.

Necessity of an International Agreement on the Analysis of Tanning Materials. By MARIUS CHOPIN, *Le Cuir*, 9, 608-10 (1920). The recent papers by Baldracco and Camilla, by Wilson and Kern, and by Scheil all show that there is no sound agreement on the present official method of tannin analysis. On the same sample of extract, using the official method, the leading leather laboratories of France, England, Belgium, Holland, and Switzerland obtained values for per cent tannin ranging from 24.9 to 28.9. This is a most serious matter in the extract market and it is urged that an international commission be appointed to review the entire subjects. J. A. W.

Insolubles in Tanning Extract Analysis. By L BLEYNIE, *Le Cuir*, 10, 57-8 (1921). The value for insoluble matter obtained by the official method is not correct because the filter paper tends to act as an ultrafilter and retains some of the tannin. Different types of paper give very different results; for the same extract one paper gave 2.0 and another paper 6.9 per cent insoluble with an equal difference, therefore, in the per cent tannin. A positive value for insoluble is obtained for a liquor already filtered clear, when it is passed through a second paper. The color of the filtrate is lighter the harder the paper used and becomes still lighter with repeated filtration. It is suggested to filter the liquor once and then filter a portion of the filtrate a second time; the drop in concentration due to the second filtration is subtracted from the drop in concentration due to the first filtration and the difference taken as a measure of the insoluble matter. J. A. W.

Weak Points in Tannin Analysis. By E. SCHELL, *Le Cuir*, 10, 107-9 (1921). Criticism made upon the method involves either the basic principle or the question of concordance. The official method gives concordant results only when the operators carry it out in a manner absolutely identical. But variations in the hide powder and the personal factor, especially in deciding when a filtrate is optically clear, lead to very large differences in the determination of tannin. A more rigid standardization of the method is essential to get concordant results. J. A. W.

Standardization of the Filtration of Tan Liquors. By E. SCHELL, *Le Cuir*, 10, 143-4 (1921). Of the several factors responsible for lack ot concordance in the official method, that requiring first attention is the method of filtration. The Berkfeld filter candle has many serious objections. A candle cannot be thoroughly cleaned and consequently the determination will be affected by the number of times the candle has been

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used and upon the nature of the liquors previously passed through it. The candle also has an undesirable influence upon the determination of the color of the filtrate. On the other hand, the candle may be preferable for certain natural quebracho extracts which would otherwise be difficult to filter. The general use of the candle has not brought about the desired concordance in the determination of insoluble. A standard filter paper, used only once and under fixed conditions, would seem to be preferable. J. A. W.

Leather Analysis. By P. CHAMBARD, *Le Cuir*, 10, 160-4 (1921). During the war the analysis of military leathers included: moisture; fat; ash; water solubles; hide substance; and combined tannin. The official form of report grouped the first four as "Non-leather substance" and the last two as "Leather Substance." The report also included fats on the absolutely dry basis; and ash, water solubles and hide substance on the fat free-moisture free basis. In reference to the work of the committee on leather analysis the author discusses the following points; sampling; determination of hide substance; and determination of water solubles; particularly for sole leather.

It is proposed that the sample be taken in the section separating the butt and neck and commonly called the shoulder strip. The piece should weigh at least 50 gms. and should be cut out at equal distance from the backbone and flank. It should be about 18 cm. long and 6 cm. wide. The advantages of this method of sampling are that the piece of leather will be of practically uniform thickness; the composition of the leather from this region is the nearest to the average composition of the whole hide; and cutting the sample does not damage the leather materially. The determination of hide substance by the Kjeldahl method, using potassium sulphite or bi-sulphate and copper sulphate, gives remarkably constant results. [*Le Cuir* 9, 294 (1920)]. It is emphasized that a sufficiently large charge, 2.8 gms., must be taken for nitrogen; 0.7 gms. is entirely too small to permit of a representative sample. The leather must be cut in cubes or slices, each being a complete section with parallel faces. The pieces need not be very thin.

The most important points in the determination of water solubles are rigidly controlled conditions with particular reference to the amount of water with a given quantity of leather; the temperature of extraction; and the time of extraction. The method for the analysis of military leathers specifies 5.0 gms. of planed leather agitated for 5 hrs. with 250 cc. of water. The extract is filtered, the first portion being rejected, and an aliquot is dried at 98°-100° C. The above proportions of sample and water are good, and the agitation gives an extract of practically constant composition after 5 hrs. The method however necessitates a certain type of agitator operating at a definite speed and also fails to define the temperature of extraction. The extraction can be easily made in the following simple apparatus. A glass or copper tube 50 mm.

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in diam. and 160 mm. high is fitted with a small copper or nickel gauze basket. A copper rod is soldered to the bottom of the basket and is cut of such a length that when the basket is filled with 5 gms. of leather and inserted in the tube containing 250 cc. of H_2O, the rod will support the basket so that the leather just is submerged. In this way the difference in gravity due to extracted matter keeps up a current in the thimble until equilibrium is reached the entire solution then being of uniform composition. At 17° C. this requires 14 hrs. but for convenience the extraction is allowed to run overnight for 16 hrs. During extraction the tube is stoppered and any desired constant temperature can be obtained by immersion of the thimbles in a suitable bath. Results have been obtained by the above method which differ but little from those at the same temperature by the agitation method. The thimble proceedure has the advantage of definitely controlled temperature for extraction and gives a means of studying different temperatures. It is believed, however, that for official analysis the ordinary temperature, that is 16°-18° C., is the most logical.

For the determination of moisture it is proposed to dry 4 gms. of leather in an air oven at 110°—115° C. As the dried leather quickly takes up moisture rapid weighing is necessary. The ash determination and the effect of magnesium sulphate on the same have been carefully studied by Jalade [*Le Cuir* 9, 467-84 (1920)].

The author is in accord with Jalade on the question of judging leather. The analysis and chemical composition of a sample of leather should not serve alone as a basis for determining the quality. The appearance and feel of the leather together with the physical tests of strength and impermeability should hold first place in its valuation. Nevertheless it must not be forgotton that only by chemical analysis can excessive loading and the like be detected. It is no doubt premature to state the composition with which a good leather of normal tannage must agree, for certainly leathers of quite defferences composition may show nearly equal quality. However, everyone who has had occasion to examine numerous samples of leather soon realizes that leathers which do not fall within certain limits are not likely to be of good quality.

R. W. F..

Blended Tanning Extracts. By GEORGES VIE, *Le Cuir*, 10, 152-5 (1921). The present demands of the tanners for extracts giving good color and finish has forced the extract manufacturers to resort to mixing different tanning materials in extract form. The suitable mixing of tanning extracts is a complex problem involving the comparative cost of the tannin unit; the selective absorption of tannin by the hide; and the partial transformation by certain mixtures of tannin into insolubles and non-tannins. Quite often the primary consideration is color and not cost and expensive materials for this reason are frequently used. The loss of tannin in mixtures has not been sufficiently studied although it has been shown that the addition of quebracho to chestnut wood lowers the absorbable material

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with an increase of insolubles. The formation of insolubles may be reduced by direct mixing of extracts without diluting them and at a temperature sufficiently high to make them readily miscible. Solid extracts should be dissolved to about 30° Bé. at 50° C. In preparing blended extracts it is most expedient to mix the different materials in the proper proportions established by analysis, and extract them in the same extractor.. To-day the material or extract serving as the basis for the blend is chestnut. An example is given in detail for a supposed blend of 20 per cent mimosa, 15 per cent myrobalans, and 65 per cent chestnut. The quantities of course being determined by proportion and figured on the charge for each extractor. Experience has shown that the average weight of wood for a 10-cubic meter extractor is 3650 kgs. A point to be considered with mixed extracts is the selective absorpton of tannin by the hide, which causes finally an accumulation or excess of one kind of tannin in the liquors. Thus in the use of mixed extracts, especially with the poorer materials such as mangrove or sulphite cellulose it is best to employ such liquors for the same stage in the process, strengthening them as required. All things considered blended extracts would appear to have a good future because they permit an economical use of tanning materials.

R. W. F.

Lactic Acid from Amylaceous Materials. By G. DESMURS, *Le Cuir* 10, 182-4 (1921). In the manufacture of lactic acid from amylaceous materials, potato or rice flour are generally used, although many other starchy materials such as low quality wheat flour, cassava, corn meal, maize may be employed. The conversation of the starch into sugar is done by malt. To 50 hectoliters of water in a vat at 45° C., are added 20 kgs. of malt, and while stirring, 1200 kgs. of flour containing 80 per cent starchy material. The temperature is then raised in ½ hr. to 70° C., after which the mass is cooled to 56° C. and 100 cc. of a milk of malt added. The mass is then maintained at 55-56° C. for about 4 hrs. and tested for complete conversion of the starch. When this is complete the temperature is raised to 80° C., and the liquid, which should have a total volume of about 60 hectoliters, is run into two fermentation vats. These vats should be closed and should be provided with coils for heating and cooling. The "must" is diluted with warm water to a content of 12-15 per cent maltose and to each vat 225 kgs. of powder chalk are added. The mixture is sterilized with live steam for 1 hr. at 95° C.; cooled to 50° C.; and seeded with a few cc. of a pure lactic ferment which has been very carefully prepared and taken from the seventh progressive inoculation of sterilized milk. After 6 to 8 hrs. the fermentation is very active and the temperature should be kept at 47-50° C. The generation of CO_2 by the lactic acid is shown by small bubbles, if these become large it is evidence of butyric fermentation, which may be confirmed at once by microscopic examination or also by calcium determination and an appreciable decrease of total acidity. The only means of preventation is by sufficient aeration of the must during fermentation. Some-

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times the presence of acetic and formic acids is noted but these should not exceed 5 per cent of the lactic acid formed. A normal fermentation should proceed rapidly the first 3 days and then it begins to decrease. When fermentation ceases and the maltose and soluble calcium content become constant it is necessary to once more sterilize the mixture allow it to cool and seed it again with the ferment. After 6 to 8 days the fermentation should be complete and not more than 0.4 per cent of unfermented maltose should remain. The calcium lactate is decomposed by an equivalent quantity of sulphuric acid. The lactic acid is concentrated in vacuum (680 mm. at 55° C.) to 50-80 per cent, in such a manner as to prevent its tranformation into lactide.

R. W. F.

Notes on Soluble Oils and Their Production. By R. SANSONE, *Le Cuir* 10, 13 and 156 (1921). The commercial soluble oils can be grouped: (1) emulsifiable oils; (2) sulfonated oils; (3) liquid soaps; (4) soluble mineral oils. Without doubt the first emulsifiable oil used in the tannery was prepared from olive oil, preferably from the olive oil of Gallipoli which always contains large quantities of free fatty acids, up to 25 and 30 per cent. In absence of this particular oil any olive oil is submitted to artificial oxidation and upon mixing with water for fat liquor forms a more or less stable emulsion. The high price and food value of olive oil, especially since by simple chemical treatment low-grade olive oils can be rendered edible, are constantly reducing the use in the tannery of this oil which in the near future will be replaced by a mixture of fatty acids and lowest grade olive oil, or simply a mixture of fatty acids with cottonseed, fish or peanut oils treated artificially to give the odor of rancid olive oil. Sulfonated oils may be classed as: (1) with castor oil base; (2) with olive oil base; and (3) with fatty acid base. Sulfonated castor oil while the best is also very expensive. Its value is often wrongly judged from the per cent fatty acids and fatty matter. This method is poor since in many cases it is easy to thus mistake for sulfonated castor oil a product made from cheaper oils. One of the first indications of genuine sulfonated castor oil is its bright color. Comparison of the melting point of the fatty acids with those from an authentic sample should be made. Rosin soaps are often used in adulteration but these can be readily detected by color and characteristic odor. Sulfonated castor oil can be easily prepared. To the castor oil add ¼ its weight of 66° sulphuric acid keeping the temperature below 35-40° C.; let the mixture stand 24 hrs., stirring it frequently; wash out most of the acid with water, siphon off the oil and neutralize remaining acid carefully with ammonia. A well prepared product upon dilution with water and addition of ammonia will remain clear. Vats for sulfonating oils are described. The vats are of hard wood and should have a capacity of 2½ to 3 times the volume of the oil to be treated. They should be provided with a gauge and with spigots at different levels for drawing off the various reaction products and wash waters. Agitation during sulfonation preferably should be done by mechanical means.

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Vats of ordinary wood should be lined with lead as otherwise the action of the acid on the wood gives a dark product. As the sulfonation generates heat, the acid should be added little at a time, taking at least an hour and the temperature should not rise above 40° C.

Sulfonated castor oils are ordinarily sold as containing 50 per cent fatty acids; sometimes oils are offered having up to 70 per cent and other times down to 33 per cent. All things considered the most suitable oils run 50 to 80 per cent fatty acids. The following tests for sulfonated oils are described. To 100 cc. of water 10 cc. of the sulfonated oil are added and the whole is agitated for some time. Upon standing a perfect emulsion should persist which should become clear upon the addition of ammonia. If the water is hard the emulsion should remain without change for an hour. To 1 liter of water are added 2½ cc. of 50 per cent acetic acid, 5 cc. of 8° Bé solution of calcium acetate and ½ cc. of a 10 per cent solution of the sulfonated oil. No change should be manifested even after boiling. To 1 liter of a solution containing 7.2 gms. of sulfuric acid (66° Bé) and 4.5 gms. of crystallized sodium sulfate is added 1 cc. of the sulfonated oil. Boiling for 1 hour should not cause any kind of separation.

For sulfonation the oil should be of good quality, free from water and the sulfuric acid should not cause any discoloration of the product. Before using any lot of acid it is best to make a complete sulphonation and fat-liquoring laboratory test of it. With the object of reducing the cost of production some manufacturers neutralize the sulfonated castor oil as soon as the acid water has been separated, thus avoiding all water washing; others reduce the quantity of ammonia required by substituting caustic soda for 4/5 of it and using the ammonia only towards the end of the operation. Castor oil has been preferred for sulfonation because in the sulfonated state it forms soluble soaps with the minimum proportion of alkali. Because of the high price of castor oil some manufacturers have returned to the use of olive or other oils; some to mixtures of olive and castor oils; and still others to fatty acids for sulfonation. Olive oil may be sulfonated as follows: 100 kgs. of oil are mixed with 20 kgs. of sulfuric acid (66° Bé) in a container of 500 liters. The mixture is allowed to stand one day and then thoroughly mixed with a solution of 10 kgs. of calcined sodium carbonate until effervescence ceases. The vat is then filled with water and left for about 2 days to clear up after which the acid water is drawn off and the oil mixed with a solution of 4 kgs. of caustic soda in 85 liters of water and neutralization is completed by the addition of ammonia to a faint alkaline reaction. Neutralization should be done at a temperature of 25°—35° C. In the above manner a sulfonated olive oil is obtained which contains 33 per cent of fatty acids. A mixture of sodium sulforicinate and olive oil is often sulfonated, although it is not as certain as separate sulfonation. The sulfonation of oleic acid is important because of the large quantities of this product as a residue from the manufacture of candles and glycerine. One of the most usual preparations is obtained by sulfonating

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260 parts of oleic acid with 90 parts of sulfuric acid for 12 hrs. The sulfo-oleic acid thus formed is left for 24 hrs., then washed with a solution of common salt and neutralized with caustic soda and ammonia. These sulfonated oils are cheap and readily soluble in water. They can be substituted for many purposes in the tannery.

Monopol soap is a special form of sulfonated oil. It is prepared sometimes by treating 100 parts by weight of castor oil with 50 parts of 66° sulfuric acid in such a manner that during the sulfonation no sulfurous acid is developed. The mixture is left to cool during 1 or 2 days with vigorous stirring from time to time. According to these proportions there are about 3 molecules of sulfuric acid for each molecule of castor oil giving thus a higher degree of sulfonation. It is upon this that the success of manufacturing depends. The temperature should be maintained between 25°-30° C. The product thus formed is then treated by one of the following procedures: To 100 kgs. of the above acid mixture, 60 kgs. of 36°—37° Bé caustic soda, are added at once while stirring. The oily mass becomes limpid and yellow. It is left for 2-3 days, during which time sodium sulphate crystallizes out. The crystals are removed and the oily mass is heated up until upon cooling it forms a soap called "Monopol." If the operations have been properly conducted and the necessary quantity of alkali correctly calculated the final product will not be acid enough to turn litmus. The second procedure is to wash each 100 kgs. of the acid mixture with 100 to 200 liters of a warm solution of common salt (25°—30° Bé) to remove the excess of acid. After thorough mixing, the mixture is left for several days and then for each 100 kgs. of the washed oil 39 kgs. of caustic soda (36°-37°) are added at once with stirring. A nearly saturated solution of common salt gives good results in promoting the formation of a solid soap. For the tannery however this is not important and the operation could be concluded after neutralization, leaving the soap in liquid form. Monopol soap is considered an acid soap of very great emulsifying power If it is heated for 4 hrs. at 100° C. and then completely neutralized a product of emulsifying power equal to that of sulfonated castor oil is obtained. A soap which dissolves completely in water may be obtained by treating a mixture of 60 parts of oleic acid with 30 parts petroleum oil with a trace of some condensation agent, such as aluminum chloride. The reaction takes place quickly at 60° C., the mass becoming solid and dark. After decanting the necessary amount of alkali is added for saponification. The reaction is based on the property of oleic acid of combining with petroleum oil in presence of a condensation agent.

R. W. F.

Tannin Analysis I. By V. KUBELKA and B. KOHLER, *Coll.* 610, 77-83 (1920). The percentage of tannin found by the shake method is usually lower than that found by the filter method. An analysis of a standard sample was made by four leather institutes and from 37 to 41 per cent tannin was found by the shake method (Official *I. A. L. T. C.*) and from 43 to 56 per cent by the filter method. In the shake method the outside of the

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hide powder particles is all tanned at once and adsorption then becomes slower. The method is suitable only for materials which are rapidly and easily absorbed. In the filter method most of the tannin is absorbed by the top layers and the bottom layers are comparatively fresh so that the detannization is more complete. The adsorption in the filter method resembles that in actual tanning more nearly than does the adsorption in the shake method. The shake method gives low results with thick or solid extract. By repeating the detannization of solid extract with fresh hide powder over 10 per cent more tannin may be removed even though the official method was followed exactly for the first detannization. The following table gives the percentage of tannin found in several tanning materials when analysed by the three methods.

	Solid quebracho extract	Liquid mimosa extract	Liquid chestnut extract	Solid chestnut extract	Liquid sumac extract
Official Shake Method	68.65	30.44	42.40	61.18	26.10
Shake Method with Double Detannization	70.74	31.44	44.20	63.00	28.90
Filter Method with Weakly Chromed Hide Powder	70.25	31.32	44.60	63.30	29.20

PERCENTAGE TANNIN IN OAKWOOD EXTRACT

	Thin liquid	Liquid	Liquid	Paste	Solid
Official Shake Method	32.6	35.5	38.4	39.8	55.90
Shake Method with Double Detannization	35.9	37.6	41.0	43.6	67.24
Filter Method with Weakly Chromed Hide Powder	36.2	37.9	41.9	45.8	68.35

[Attention should be called to the treatise on the Relative Value of the Hide powder Filter and the American Shake, or Chromed Hide Powder Method of Tannin Analysis, This JOUR. 1, 288 (1906), which adequately covers this phase of the question. Ed.]

I. D. C.

Mineral Tannage IV. By W. MOELLER, *Collegium* 610, 67-75 (1921). An investigation of the tanning action of iron salts similar to that for chromium salts [see *Coll.* 608, 522 (1920)]. 4.4 grams portions of hide powder were treated with 100 cc. portions of ferric chloride solutions of concentrations of 1, 3, 5 and 10 per cent and analyzed after 1, 3 and 8 days and 1 and 3 months. A similar series of experiments was made using neutralized instead of pure ferric chloride solutions. The adsorption of pure ferric chloride was almost constant for the first eight days, but then increased continuously until the experiment was completed. The adsorption would apparently have continued indefinitely if the time had

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been extended. The adsorption of neutralized ferric chloride was more rapid than the adsorption of the unneutralized but neither in this case was an end point in the absorption reached. A large amount of hide substance dissolved in the pure ferric chloride solution, the largest amount being 67.6 per cent in the 10 per cent solution after 3 months. In this case the hide substance remaining had absorbed 80 per cent of ferric chloride. In the neutralized ferric chloride solution the dissolved hide substance was constant, below 1.5 per cent, for the first 8 days, but then increased, showing that a true tanning system was not present. A series of experiments in which 1000 cc. portions instead of 100 cc. portions of ferric chloride were used is not yet complete. Less ferric chloride was absorbed in one month than in one day, but the explanation of this is not known. The dissolved hide substance was practically 3 per cent in every case, with both the neutralized and the unneutralized ferric chloride. In conclusion the author states that the usual explanation of the instability of iron tanned leather, that it is due to oxidation is not correct since intact hide substance is very difficult to oxidize. Iron salts have a strong tendency to ionize and the ions, especially hydrogen ion, cause hydrolysis of the hide substance in the leather. Organic salts are beneficial since they repress this hydrolysis. The slight tanning action of unneutralized iron and chromium salts is due to the fact that the hydrolysed hide substance acts as an alkali, neutralizing a small amount of the salt and thus setting up a peptized or tanning system.

I. D. C.

PATENTS.

Tanning. British Patent 155,887. C. F. L. BARBER and P. R. BARBER, Yorkshire. Sept. 16, 1919. A chrome tanning-liquor is prepared by the action of synthetic tans upon a solution of chrome acid or a bichromate and acid solution.

Making Leather. British Patent 156,079. O. ROHM, Darmstadt, Germany. Oct. 12, 1920. Relates to process for the depilation, neutralization, and bating of hides and skins by means of pancreatic enzymes after a short preliminary treatment with an alkaline solution, and consists in adding a salt of an alkali or alkaline earth to the alkaline solution in order to obviate stiffness and over-plumping.

Tanning. British Patent 156,186. CHEMISCHE FABRIKEN WORMS AKT. GES., Frankfurt-on-Main, Germany. Jan. 3, 1921. A tanning process consists in the use of mixtures of heavy metal salts of lignin-sulphonic acids from waste sulphite liquors, with salts of other organic or inorganic acids such as sulphuric, formic, lactic acid, &c., and with or without addition of other tanning or non-tanning agents. The mixed salts precipitate glue and are stated not to flocculate in dilute aqueous solutions.

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Synthetic Tanning-Agents. British Patent 156,254. CHEMISCHE FARBIKEN & ASTHALTWERKE ART.-GES., Grieshein-on-Main, Germany. Jan. 4, 1921 Synthetic tanning-agents consisting of coupled aromatic compounds, and vegetable tanning-agents, are converted into aluminium or chromium salts, which also are tanning-agents, by treating the free acids or their salts, or mixtures thereof, with aluminium or chromium compounds, or mixtures thereof.

Emulsions. British Patent 156,546. L. STEIN, Fulda Germany, Jan. 5, 1921. Oils, resin, and other substances insoluble in water are emulsified by mixing their solutins in inert organic liquids (benzine, benzene, carbon tetrachloride, &s.) with excess of concentrated waste sulphite cellulose liquor. The products can be used for tanning, for dressing cloth, or as agglutinants.

Extraction of Glue and Fats. British Patents 156,645, 156,646 and 156,647. K. NIESSEN, Pasing, near Munich, Germany. Jan. 6, 1921. Methods of extracting glue from bones, gristle, leather waste, animal skins, fish waste, etc.

Tannic Extracts. British Patent 156,653. RIALLAND, A. A. A. M. J. M. E. H., Rennes, Ille et Vilaine, France. Jan. 6, 1921.

Tannin-containing materials (wood, bark, or leather) are extracted by alkali solutions, from the filtered extract the tannin is precipiated as an insoluble metal tannate, which is then decomposed by an acid, such as sulphuric or oxalic; a reducing-agent such as a sulphite may be added in the alkali extraction to prevent oxidation of the tannin, or the extraction may be performed in a non-oxidizing atmosphere. When treating sawdust or shavings, any alkali-cellulose formed is precipitated by neutralizing the alkaline extract by an acid, before precipitation of the metal tannate.

Tanning-agents. British Patent 156,669. CHEMISCHE FABRIKEN Worms AKT.--GES., Frankfurt-on-Main, Germany. Jan. 6, 1921. Tar phenols of boiling-point 185-200° C. are heated with sodium sulphite and formaldehyde solution, the product acidified with sulphuric acid and the sulphur dioxide boiled off, and the product finally neutralized with ceric hydroxide; a mixture of napthalene and phenol is sulphonated and condensed with formaldehyde solution, and the product is further condensed with tannin and formaldehyde solution, and finally neutralized with potash and ceric hydroxide. The products may be used in tanning alone or mixed with other tanning-agents.

Tanning. British Patent 156,670. CHEMISCHE FABRIKEN WORMS AKT.-GES., Frankfurt-on-Main, Germany. Jan. 6, 1921.

Hides are tanned with the heavy metal salts (other than aluminium chromium salts) of synthetic tanning-agents of the kinds described above.

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Leather-working Machines. British Patent 157,085. MASCHINENFABRIK TURNER AKT.-GES., Frankfurt-on-Main, Germany. Jan. 8, 1921.

Relates to work supporting rolls for leather-working machines.

Leather-splitting Machines. British Patent 157,086. MASCHINENFABRIK TURNER AKT.-GES., Frankfurt-on-Main, Germany. Jan. 8, 1921.

Leather-working Machines. British Patent 157,087. MASCHINENFABRIK TURNER AKT.-GES., Frankfurt-on-Main, Germany. Jan. 8, 1921.

Relates to a draw roller for drawing hides.

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The American Leather Chemists Association

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BI-ANNUAL CONFERENCE OF THE SOCIETY OF LEATHER TRADES' CHEMISTS

176 Tower Bridge Rd.
London, S. E. 1
13th July, 1921

Dear Mr. Reed:

On behalf of the Executive Committee of the Society of Leather Trades' Chemists, I have very much pleasure in conveying to your President, Council and members of the American Leather Chemists Association our hearty greetings, and also an

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invitation to any of your members to attend the bi-annual conference of our Society to be held in the Hall of the Leathersellers' Company, St. Helen's Place, Bishopsgate, London, E. C. 3. I sincerely hope that some members of your association will be able to attend, and I hope that in addition some of your members will send over some scientific papers to be read and discussed.

We trust that, as in the past, our two associations may work together in cordial co-operation. Our aims are the same, although our methods may slightly differ, but we are both working to elucidate the scientific principles underlying the great leather industry.

With cordial greetings,

Believe me,

Yours very truly,

(Signed) J. Gordon Parker

President.

The Secretary,
American Leather Chemists Association,
New York.

SAMPLING OF LEATHER AND ITS PREPARATION FOR ANALYSIS—COMMITTEE REPORT, 1921.

By F. H. Small, Chairman

Committees to study the sampling and preparation for analysis of several classes of leather were appointed by the 1919-20 Council. These committees, as a whole, did little more than make a preliminary survey of the question, but they did arrive at the conclusion that any adequate discussion of the subject must be based on analyses of whole skins or hides or at least sides of leather.

The 1920-21 Council combined these several committees into one, requesting the one committee to cover the whole field and the members who actually participated in the work were W. K. Alsop, A. C. Orthmann, J. S. Rogers, J. M. Seltzer and F. H. Small, Chairman.

Orthmann made a study of light leathers, Alsop analyzed a side of sole leather, Rogers a side of rough belting leather, Seltzer a side of union sole leather and Small a side of tanned and curried belt leather.

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An outline of the work undertaken is contained in the following directions sent out by the Chairman.

"You have signified a willingness to serve on this Committee and the purpose of this letter is to put before you an outline of the method of study which appeals to your chairman as desirable so that you may suggest any changes which you think should be made, and that final instructions may be issued which embody the best thought of all the members of the Committee.

Before we can determine whether a sample is representative, it is essential that we know the average composition of the thing sampled as well as the composition of the sample. In sampling a belly, a back, a shoulder, it is therefore necessary to know the analysis of the belly, back or shoulder as a whole, before we can say that any sample which we take is representative.

You will find enclosed a diagram showing a half hide mapped into sections. An attempt has been made to so map the hide that the composition of the leather in each section will be as uniform as is possible without having an excessive number of sections, and also so that some of the sections will be so located and of such a size that they may be useable in a practical method of sampling. Your criticism is invited on the mapping, bearing in mind that the diagram is supposed to show a steer hide and that some modification by way of reducing the number of sections may be necessary when applying this mapping to small hides or skins.

The idea is, that the leather to be studied shall be a whole half hide or skin; that it shall be cut into pieces as shown in the diagram; that each piece shall be weighed; the whole of the piece prepared for analysis; and an aliquot sample analyzed. In this way we shall secure the analysis and weight of each section and so shall be able to calculate the analysis of any combination of sections we may care to make, up to a whole half hide. Knowing the analysis of the back or shoulder, etc., and of its component sections, we may hope to devise a method of sampling which will be at once accurate and practicable. This, of course, is our ultimate object and is the conclusion to be drawn by you from your work.

Following is a suggestion for the analytical procedure to be followed and here again your comments looking to the securing of the most satisfactory and accurate methods are invited. The

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essential points are, that the methods employed shall give results which duplicate satisfactorily and that exactly the same procedure shall be followed in the analysis of every section.

Preparation of Sample: This JOUR., Vol. XIII-232; Vol. XIV-321.

All samples for analysis should be reduced to a fine state of subdivision preferably being sawed, using a series of at least three saws, rip-saw type, diameter of from 8 to 10 inches, with staggered teeth and at an approximate speed of 2500 to 3000 R. P. M. The best samples seem to be obtained by using this method and it is therefore recommended.

All samples should be put into air-tight containers immediately after preparation. If no sawing apparatus is available, the samples should be planed to as fine a state as possible. In the case of skins too light to be sawed or planed, cut into as small pieces as practical.

The analysis of the prepared samples should include:

Water:

Dry 10 grams of leather for 16 hours at a temperature between 95° and 100° C. (Official Method.)

Fats: This JOUR., Vol. XIII-138, Vol. XIV-140, Vol. XIV-499 and 507.

Extract 30 grams air-dry leather in Soxhlet apparatus until free from grease, using redistilled petroleum ether boiling below 80° C. The extraction should continue for at least 6 hours, preferably over night. Evaporate off solvent and dry to approximate constant weight at 95° to 100° C.

It is recommended that the leather after extraction with petrol. ether be re-extracted using chloroform, thus giving a measure of the material untouched by ether but extracted by chloroform. Remove leather from extractor, spread out to dry and use dried leather for water-soluble extraction.

Water-Soluble: This JOUR., Vol. XIV-488.

Digest 30 grams grease-free leather with distilled water at room temperature over night in an apparatus embodying a percolator

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surrounded by a water jacket which can be kept at a desired temperature. Extract with water at 50° C. keeping the water jacket at 50° C. also. Extract for 3 hours to a total volume of two liters. It is recommended that a water-soluble determination be made both on the original leather and on the grease-free leather and the difference in extraction noted.

Digestion before extraction is optional as both methods have many adherents. Whatever type of extractor used, all extractions should be made in exactly the same manner so as to avoid variations due to manipulation.

Determine the following in the extractive solution:

Total Solids and Non-tannin—as in Official Method for extract analysis.

Ash: This Jour., Vol. XIV-243, Vol. XIV-443, Vol. XV-130.

Evaporate 500 c. c., water soluble solution to small bulk, transfer to tared Pt, porcelain, or silica dish, evaporate to dryness, ignite at dull red heat until free from carbon. Call this "soluble ash."

Remove extracted leather from percolator, air dry, then dry in oven at 98° to 100° C., cool and weigh. Mix thoroughly, and ignite ⅓ thereof at a dull red heat until free from carbon. Call this "insoluble ash." The sum of the two ash figures is the total ash.

Epsom Salts: Combine the soluble and insoluble ash, procured as above, or ash a fresh portion of leather (10 grams) and determine Mg. as follows:

Take up with HCl plus H_2O, heat, wash into 300 cc. beaker, add 25 cc. of 10 per cent NH_4Cl, heat to boiling, add 20 cc. of 5 per cent oxalic acid and slowly add ammonia until slightly alkaline. Let stand ½ hour, filter, wash thoroughly and determine Mg in filtrate.—If any considerable amount of Mg comes down with the iron, aluminum and calcium, it will be necessary to take up the precipitate with a little HCl, reprecipitate and add the filtrate from this precipitation to that first obtained.

To determine the Mg, acidify the condensed combined filtrate with HCl. Immediately add 30 cc. NH_4OH, allow to cool, add 5

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cc. NH_4OH more, let stand 4 to 5 hours, filter, wash with 2.5 per cent NH_4OH until free from chlorides. Dry and ignite in Pt crucible, slowly at first, until ppt. is white. Cool, weigh as $Mg_2P_2O_7$. Calculate per cent $MgSO_4 . 7H_2O$ in original leather.

Sugars: Official Method A. L. C. A. 1919, Jl., Vol. XIV-665.

Use toluol as preservative for water solubles solutions. In working with leathers of a high epsom salts content, it is recommended that neutralization after hydrolysis be made with a concentrated solution of NaOH, using only such excess as is required to ppt. Mg. and taking special care to make removal of lead before hydrolysis as complete as possible. For leather extracts containing negligible quantities of epsom salts it is recommended that Na_2CO_3 be used as neutralizing agent.

Nitrogen: Official Method A. L. C. A. 1919, Jl., Vol. XIV-666.

Digestion of leather with K_2SO_4 is aided considerably by adding 1.0 gm. $CuSO_4$, the $CuSO_4$ acting as a catalyzer and shortening the digestion time considerably."

The mapping and analytical outline suggested above were approved by the committee and were used in the work. No special study was made of the method of preparing the leather for analysis, nor of the analytical methods followed, the attention of the committee being confined wholly to the sampling phase. So far as preparation, mode of analysis, soundness of method, etc., are concerned it seems probable that the methods of preparation used and the analytical methods employed were capable of producing results that were twice alike, inasmuch as considerable of the work was done in duplicate and the duplicate determinations agreed within the usual limits of error accepted for work of the sort in question. Furthermore the final figures have every indication of being comparable.

If then we assume for the sake of argument that the method for water-solubles needs revision, this yet is of no material interest in the present investigation provided that the method used gave comparable results capable of duplication and this we believe to have been the case.

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Discussion of details of methods of preparation and analysis seem, therefore, unnecessary and this phase of the subject will not be considered further beyond remarking that the methods described are those which have received the sanction of the Association and seem the most desirable.

In connection with the investigation there seemed an opportunity for securing, without much extra labor, data on one or two moot questions, in particular the use of chloroform as a solvent for the extraction of grease and the effect on the "water-solubles" figure as determined by the present official method of using leather before and after grease has been extracted. Accordingly tests, bearing on this question, were suggested to the members as noted above and several did some work along these lines. Orthmann reported "I collected all the chloroform extraction of the first calf skin I analyzed, combined the whole and made a qualitative examination. Result: Heavy grease, chrome soap, black dye and a transparent, glutinous substance that appeared to swell slightly upon adding chloroform, but did not go into solution with that solvent (although being extracted with that solvent). This latter substance comprised at least 50 per cent, the grease coming next followed by the dye and finally the soap."

J. S. Downing, who did the analytical work in the Chairman's laboratory, and to whom his thanks are due for much valuable assistance in connection with the committee work, extracted various of the leather samples with chloroform after extraction with petroleum ether and obtained the following results:

Sample No.	Total* Chloroform	Fatty matter soluble in petroleum ether		Oxidized fatty acids		Tannin	
		Per cent*	Per cent of total extract	Per cent*	Per cent of total extract	Per cent*	Per cent of total solids
2	.86	.04	4.6	.50	58.1	.32	37.3
4	1.03	.05	4.6	.60	58.1	.38	37.3
11	1.65	.57	34.5	.59	35.8	.49	29.7
18	1.56	.54	34.5	.56	35.8	.46	29.7
24	1.66	.07	4.2	1.09	65.4	.50	30.5
26	1.74	.07	4.2	1.14	65.4	.53	30.5
31	1.37	.09	6.7	.84	61.5	.44	31.8
34	1.35	.09	6.7	.83	61.5	.43	31.8

*—Per cent of original leather.

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Alsop reported as follows:

Sample	Petroleum ether extract	Chloroform extract
1	5.78	2.15
2	4.93	2.34
3	4.48	1.89
4	3.78	1.77
5	2.97	1.56
6	3.16	1.49
7	2.79	1.93
8	5.10	2.03
16	8.23	1.26
18	8.02	1.79
19	2.92	1.27
20	2.77	1.12
21	2.65	1.35
22	3.80	1.12
23	4.87	1.61
24	5.17	1.09
25	3.06	1.26
27	2.11	.62
28	2.02	.64
29	2.63	.34
30	3.54	1.21
31	2.49	.56
32	2.81	.99
33	2.39	.94

You will note that the amount extracted by chloroform varies a good deal in these samples. They were run in three sets of eight. The results from the first set are higher than those from the second and those from the second are higher, generally speaking than the results from the third. They were all extracted the same length of time with redistilled chloroform. We combined the residues from these 24 determinations (representing 250 grams of leather) obtaining about three grams of residue equal to 1.3 per cent. On trying to dissolve this extract we found that only a portion of it was soluble in chloroform equal to about 38 per cent of the total. The balance was soluble in cold alcohol and the greater portion soluble in water. The amount of actual fatty matter found in the total extract was:

Unsaponifiable	7.5 per cent
Fatty acid soluble in petroleum ether	9.7 per cent
Oxidized fatty acid	6.0 per cent
	23.2 per cent

Hence any amount of fatty matter removed by chloroform subsequent to the petroleum ether extraction, in this particular in-

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stance, amounted to about .3 per cent of the weight of the leather. The remainder, about 1 per cent, seemed to be principally tanning material as shown by qualitative tests and the characteristics of the residue. The tests clearly showed the presence of tannin."

The only work done to determine the variation in the water-solubles figure due to extraction before and after the removal of the grease from the leather was by Downing, who obtained results as follows:

WATER SOLUBLES

Sample No.	Original* leather	Grease free* leather	Grease in original leather
1	10.15	12.86	12.4
2	9.21	12.94	11.07
3	10.74	13.39	9.62
4	9.85	11.29	11.78
11	10.30	16.71	21.17
18	9.04	13.45	22.86
24	13.46	14.83	16.30
26	11.39	14.14	20.50
31	10.50	12.84	21.79
34	9.37	12.58	20.33

*—Figured on grease and moisture free leather.

In assembling the results secured by the various members of the committee, the fact that the leathers were of such different types made compilation of the results in one table confusing rather than helpful to the understanding and interpretation of the figures. There was only one item that was at all comparable, namely the hide-substance figure, and in order to present a somewhat composite picture of the varying composition of a hide, as well as to bring out the point that the variation in composition of the finished leather is similar regardless of the particular mode of tanning and finishing, a diagram was prepared showing the hide substance figure found by each analyst in the several cuttings into which the side tested by him was divided. Other than this the results secured by the several collaborators appear in diagrams and tables showing the work the individual collaborator did. These are as follows:

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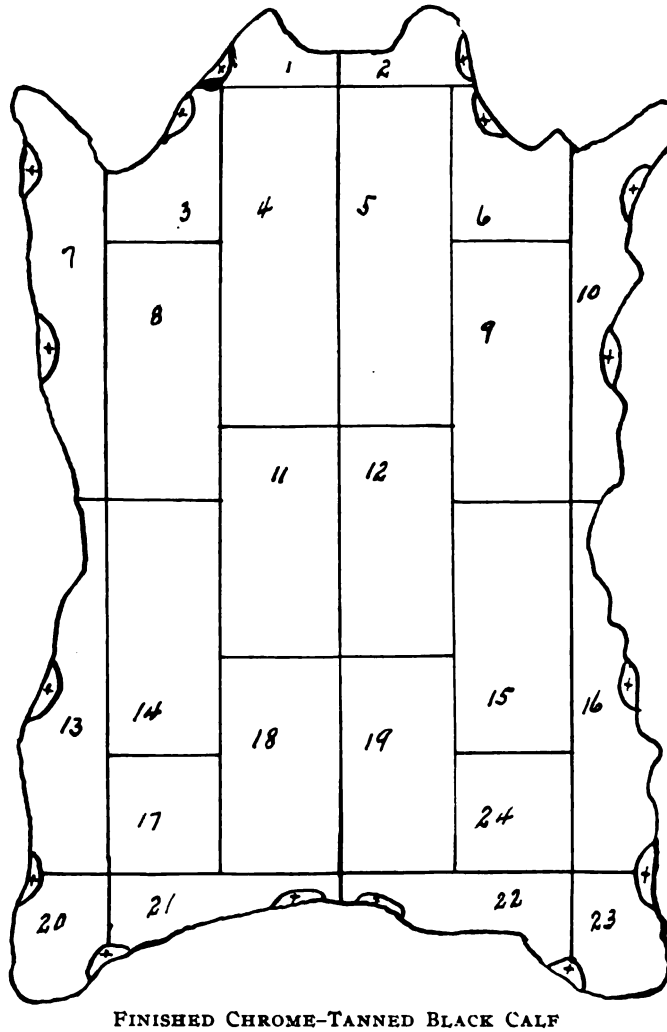

FINISHED CHROME-TANNED BLACK CALF

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Finished Chrome-Tanned Black Calf Leather

Section Number	Weight in grams	Per cent. of total weight	Size of cutting	Moisture Per cent.	Petrol fat Per cent.	Ash Per cent.	Chrome Per cent.	Sulfates Per cent.	Hide substance Per cent.
1	16	4.26	6.5″	11.48	13.40	6.05	3.41	2.52	59.61
2	10	2.66	6.5″	11.21	14.34	5.70	3.45	1.95	62.35
3	10	2.66	5.0 x 6.0 x 7.0″	12.04	12.96	5.70	3.65	2.68	62.44
4	23	6.12	5.0 x 14.0″	12.94	11.17	5.83	3.68	2.53	60.61
5	23	6.12	5.0 x 14.0″	13.68	11.50	5.73	3.74	2.07	62.45
6	9	2.39	5.0 x 7.0″	12.07	14.95	5.45	3.62	2.41	59.51
7	16	4.26	1.5 x 16.0″	13.33	12.40	6.08	3.89	2.58	62.38
8	18	4.79	5.0 x 10.0″	13.03	11.49	5.90	3.81	2.46	63.16
9	18	4.79	5.0 x 10.0″	13.32	12.18	5.81	3.66	2.75	62.88
10	17	4.52	1.5 x 14.0″	12.57	13.46	5.83	3.63	2.68	60.35
11	16	4.26	5.0 x 10.0″	12.64	10.38	5.91	3.77	2.25	60.40
12	16	4.26	5.0 x 10.0″	12.89	11.55	5.84	3.61	3.04	62.56
13	11	2.93	4.0 x 13.0″	12.28	11.11	5.97	3.75	2.89	61.14
14	18	4.79	5.0 x 10.0″	13.97	9.76	5.90	3.95	2.75	62.35
15	18	4.79	5.0 x 10.0″	12.88	11.43	5.66	3.68	2.61	63.05
16	10	2.66	4.0 x 13.0″	12.28	12.43	5.93	3.78	2.82	63.54
17	9	2.39	5.0 x 5.0″	13.74	9.11	5.83	3.88	2.80	64.68
18	14	3.72	5.0 x 9.0″	13.42	9.98	5.89	3.83	3.19	62.95
19	14	3.72	5.0 x 9.0″	13.19	10.12	5.95	3.82	2.42	63.27
20	12	3.19	4.0 x 5.5″	13.16	11.39	5.88	3.99	2.06	60.76
21	15	3.99	10.0 x 5.5 x 2.5″	12.62	10.02	6.04	3.96	2.77	59.89
22	16	4.26	10.0 x 2.5 x 6.0″	12.78	10.68	5.76	4.00	2.75	60.50
23	10	2.66	4.0 x 6.0″	13.54	12.36	6.09	3.97	2.46	61.03
24	9	2.39	5.0 x 5.0″	12.93	10.44	5.61	3.90	3.12	62.58
*x	28	7.45		12.40	11.92	5.88	3.82	2.57	59.74
Average					11.57	5.86	3.97	2.60	61.69

*x equals P. and V. method of sampling. Analysis calculated on 12 per cent. moisture basis.

Aug. C. Orthmann,
Chemist.

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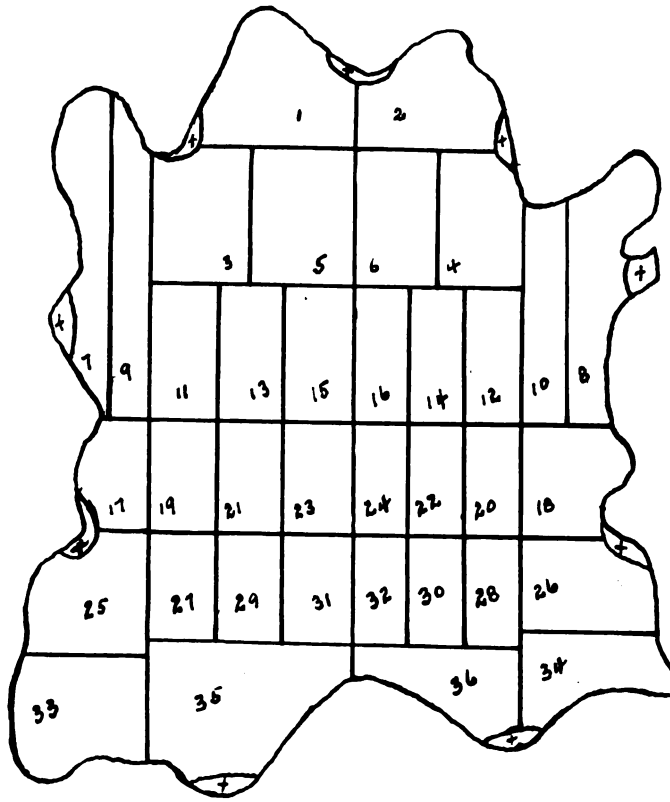

FINISHED CHROME-TANNED BLACK CALF

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FINISHED CHROME-TANNED BLACK CALF LEATHER

Section Number	Weight in grams	Per cent. of total weight	Size of cutting	Petrol fat Per cent.	Ash Per cent.	Chrome Per cent.	Sulfates Per cent.	Hide substance Per cent.
1	15	3.09	9.0 x 4.0″	6.77	5.26	3.70	3.26	68.34
2	18	3.70	8.0 x 4.0″	6.64	4.80	3.57	3.19	69.30
3	16	3.29	6.0 x 8.0″	7.34	5.66	3.83	3.14	67.34
4	15	3.09	5.0 x 8.0″	8.23	6.05	3.93	3.18	65.86
5	17	3.50	6.0 x 8.0″	6.73	6.21	4.03	3.47	66.84
6	16	3.29	5.0 x 8.0″	7.37	5.97	4.03	3.74	67.34
7	14	2.88	1.5 x 12.5″	9.68	6.23	4.12	3.61	63.90
8	15	3.09	1.0 x 12.5″	10.16	6.17	4.12	3.03	62.91
9	10	2.06	2.5 x 12.0″	9.20	5.98	4.12	3.29	62.91
10	12	2.46	2.5 x 12.5″	10.44	6.55	4.22	2.93	60.95
11	13	2.67	4.0 x 8.5″	7.79	5.58	4.06	3.69	63.90
12	11	2.26	3.5 x 8.5″	8.24	5.55	3.96	2.91	63.90
13	12	2.47	4.0 x 8.5″	6.88	5.74	3.99	3.62	65.86
14	10	2.06	3.5 x 8.5″	6.84	6.04	3.99	3.53	64.88
15	12	2.47	4.0 x 8.5″	7.56	5.67	3.86	3.45	67.34
16	11	2.26	3.5 x 8.5″	7.17	5.97	3.99	3.38	65.86
17	12	2.47	4.5 x 8.5″	7.18	5.99	3.99	3.45	64.88
18	14	2.88	7.0 x 8.5″	9.21	5.86	3.93	3.17	63.90
19	12	2.47	4.0 x 7.5″	7.64	5.31	3.83	3.28	66.35
20	10	2.06	3.5 x 7.5″	7.23	5.71	3.80	3.50	64.88
21	12	2.47	4.0 x 7.5″	6.22	5.23	3.61	2.87	67.34
22	10	2.06	3.5 x 7.5″	6.48	5.29	3.70	3.41	68.32
23	12	2.47	4.0 x 7.5″	6.07	5.41	3.74	3.48	68.32
24	10	2.06	3.5 x 7.5″	5.96	5.33	3.74	3.81	69.36
25	16	3.29	7.0 x 7.0″	8.96	6.27	4.22	3.64	64.88
26	12	2.47	8.0 x 5.5″	11.16	5.80	4.06	2.62	62.91
27	12	2.47	4.0 x 7.5″	7.26	5.76	3.96	3.54	66.84
28	9	1.85	3.5 x 7.5″	7.70	5.55	3.74	3.64	65.86
29	12	2.47	4.0 x 7.5″	6.80	5.66	3.90	3.51	69.36
30	10	2.06	3.5 x 7.5″	6.52	5.57	3.80	3.57	69.79
31	12	2.47	4.0 x 7.5″	7.23	5.92	3.99	3.64	69.79
32	10	2.06	3.5 x 7.5″	7.42	5.75	3.99	3.72	69.79
33	14	2.88	7.0 x 7.0″	8.85	6.39	4.35	3.45	63.90
34	12	2.47	8.0 x 7.0″	10.56	6.24	4.19	3.38	64.88
35	22	4.53	12 x 7.5 x 2.0″	7.66	6.28	4.25	2.80	66.35
36	15	3.09	10 x 5.0 x 2.0″	7.83	6.11	4.15	3.75	67.83
*x	22	4.53		10.31	5.87	4.03	2.80	62.43
Average				7.96	5.74	3.98	3.34	66.20

*x equals P. and V. method of sampling.

Analysis calculated on 12 per cent. moisture basis.

AUG. C. ORTHMANN,
Chemist.

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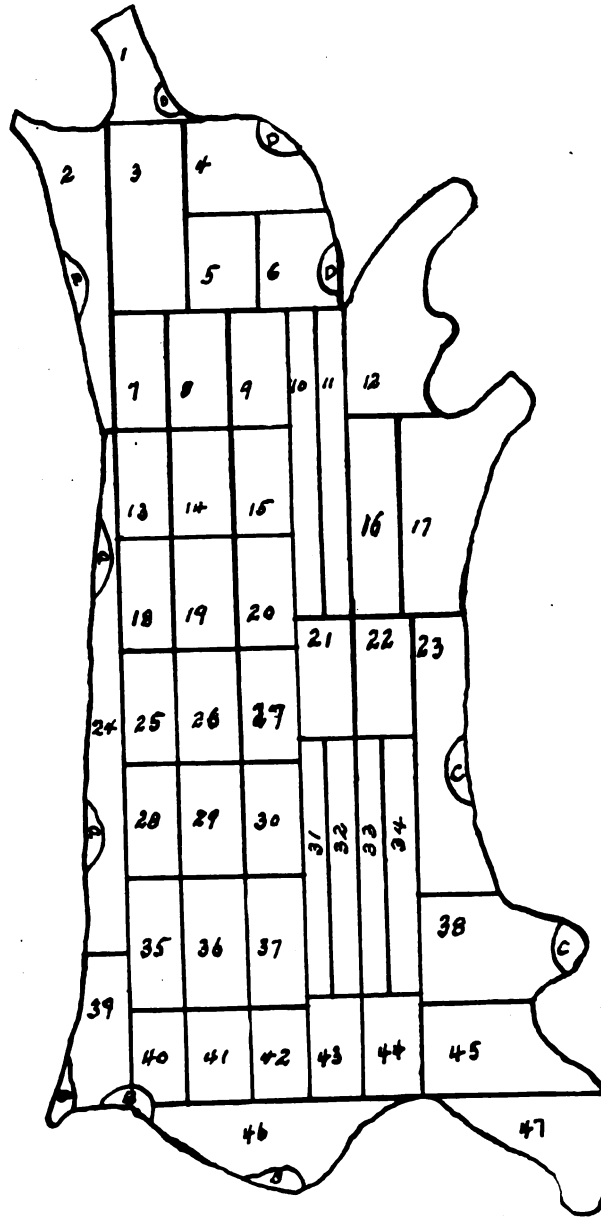

FINISHED CHROME-TANNED BLACK KIP-SIDE

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Finished Chrome-Tanned Black Kip Side Leather

Section Number	Weight in grams	Per cent. of total weight.	Size of cutting.	Petrol fat Per cent.	Ash Per cent.	Chrome Per cent.	Sulfates Per cent.	Hide substance Per cent.
1	28	3.24	5″	9.89	4.87	3.00	1.26	67.84
2	18	2.08		9.82	4.61	3.22	1.66	67.34
3	32	3.70	5.0 x 12″	9.87	4.45	3.33	1.26	67.84
4	13	1.50	10.0 x 5″	10.99	5.00	3.33	1.20	64.88
5	14	1.62	5.75 x 6″	11.31	4.56	3.33	1.01	62.42
6	11	1.27	6.0 x 6″	11.60	5.15	3.38	1.21	62.91
7	17	1.97	4.0 x 8″	10.49	4.53	3.22	1.50	66.35
8	14	1.62	4.0 x 8″	10.29	4.41	3.11	1.34	67.84
9	12	1.39	4.0 x 8″	9.64	4.53	3.38	0.92	71.27
10	18	2.08	2.0 x 19″	9.14	4.58	3.11	1.39	69.31
11	18	2.08	2.0 x 19″	8.38	4.58	3.59	0.87	67.84
12	32	3.70	5.25 x 8.5″	9.16	4.77	3.38	1.09	66.85
13	15	1.73	4.0 x 8.0″	9.32	4.36	3.11	0.90	65.86
14	16	1.85	4.0 x 8.0″	8.16	4.20	3.16	1.56	68.33
15	17	1.97	4.0 x 8.0″	6.78	4.31	3.11	1.36	70.78
16	13	1.50	3.0 x 11.0″	8.93	4.75	3.38	0.87	67.84
17	31	3.58	3.25 x 11.0 x 2.0″	8.44	4.75	3.38	1.33	66.35
18	18	2.08	4.0 x 8.0″	6.76	4.17	3.16	1.69	68.82
19	20	2.31	4.0 x 8.0″	5.78	4.11	3.22	1.11	72.25
20	18	2.08	4.0 x 8.0″	6.41	4.35	3.27	1.38	73.23
21	19	2.20	4.0 x 10.0″	7.64	5.08	3.27	1.04	68.82
22	17	1.97	4.0 x 10.0″	7.33	5.02	3.27	1.09	64.88
23	17	1.97	4.0 x 21.0 x 2.25″	8.96	5.06	3.38	0.98	65.37
24	29	3.35	3.0 x 35.0″	8.01	4.27	3.38	1.58	67.84
25	19	2.20	4.0 x 8.0″	6.83	4.33	3.33	1.61	73.73
26	19	2.20	4.0 x 8.0″	5.74	4.37	3.27	1.51	69.31
27	15	1.73	4.0 x 8.0″	8.32	4.62	3.43	1.16	68.33
28	19	2.20	4.0 x 8.0″	6.59	4.38	3.48	1.58	73.73
29	19	2.20	4.0 x 8.0″	5.81	4.46	3.43	1.63	69.80

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FINISHED CHROME-TANNED BLACK KIP SIDE LEATHER (Continued)

Section Number	Weight in grams	Per cent of total weight	Size of cutting	Petrol fat Per cent	Ash Per cent	Chrome Per cent	Sulfates Per cent	Hide substance Per cent
30	17	1.97	4.0 x 8.0"	7.23	5.06	3.70	1.39	68.33
31	14	1.62	2.0 x 16.0"	9.04	5.29	3.53	1.26	67.84
32	13	1.50	2.0 x 16.0"	9.12	5.56	3.64	1.08	65.86
33	11	1.27	2.0 x 16.0"	10.03	5.33	3.53	0.91	64.88
34	12	1.39	2.0 x 16.0"	9.36	5.30	3.59	0.90	63.40
35	19	2.20	4.0 x 8.0"	6.52	5.07	3.64	1.61	71.76
36	18	2.08	4.0 x 8.0"	6.78	5.40	3.70	1.44	69.80
37	17	1.98	4.0 x 8.0"	6.00	5.02	3.70	1.57	67.84
38	19	2.20	7.0 x 8.0 x 4.0"	9.41	5.52	3.70	0.95	62.91
39	20	2.31	3.5 x 12.0"	8.12	4.71	3.59	1.58	66.35
40	13	1.50	4.0 x 5.75"	7.57	5.38	3.27	1.68	70.78
41	12	1.39	4.0 x 5.75"	6.40	5.22	3.70	1.43	67.84
42	10	1.16	4.0 x 5.75"	8.30	4.72	3.48	1.13	67.84
43	18	2.08	4.0 x 8.0"	6.12	4.92	3.43	1.52	69.31
44	17	1.97	4.0 x 8.0"	7.86	4.62	3.48	1.45	69.31
45	22	2.54	10.0 x 5.75 x 7.25"	7.97	4.51	3.59	1.17	67.34
46	15	1.73	12.0"	7.85	4.74	3.59	1.35	67.34
47	26	3.01	14.0"	9.18	4.44	3.48	1.24	67.84
*X	24	2.66		8.91	4.71	3.43	1.63	66.85
Average				8.25	4.72	3.41	1.32	68.98

*x equals P. and V. method of sampling. Analysis calculated on 12 per cent. moisture basis.

AUG. C. ORTHMANN,
Chemist.

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Finished Black Chrome-Tanned Kip Leather

Section Number	Weight in grams	Percent of total weight	Size of cutting	Moisture Per cent.	Petrol fat Per cent.	Ash Per cent.	Chrome Per cent.	Sulfates Per cent.	Hide substance Per cent.
1	25	2.12	8.0″	11.99	9.25	6.06	4.57	3.36	60.55
2	17	1.44	6.0″	11.84	12.98	5.61	4.44	3.27	61.02
3	38	3.22		10.82	9.96	5.59	4.54	3.74	66.57
4	25	2.12		11.35	9.45	5.54	4.57	3.78	66.45
5	18	1.53	8.0″	12.13	10.57	6.11	4.86	3.67	65.04
6	25	2.12	2.5 x 13.0″	12.20	11.78	6.01	4.77	3.41	63.74
7	20	1.69	5.75 x 15.0″	11.98	8.48	5.45	4.51	4.46	67.87
8	30	2.54	6.0 x 15.0″	11.78	8.80	5.33	4.64	3.98	68.92
9	26	2.20	4.5 x 15.0″	11.05	9.90	5.56	4.67	3.45	65.04
10	34	2.88	5.75 x 15.0 x 2.5″	9.56	11.04	5.54	4.70	3.75	66.80
10 a	26	2.20	3.5 x 15.0″	10.77	8.23	5.69	4.70	3.75	68.46
11	19	1.61	8.5″	10.93	9.24	5.81	4.67	4.09	67.04
11 a	13	1.10	3.0 x 15.0″	11.31	9.76	5.87	4.89	3.56	63.37
11 b	25	2.12	3.0 x 15.0″	11.34	8.02	5.30	4.60	3.89	68.10
11 c	16	1.36	3.0 x 11.25″	11.16	8.29	5.53	4.60	3.49	66.10
12	14	1.19	7.5 x 6.0 x 4.0″	10.59	11.68	5.47	4.54	3.56	65.04
13	26	2.20	7.5 x 6.0″	11.68	8.59	5.49	4.54	3.68	66.69
14	25	2.12	7.5 x 6.0″	12.03	9.31	5.49	4.38	3.55	66.33
15	26	2.20	15.0 x 3.0″	11.04	6.83	5.42	4.44	3.98	69.87
16	25	2.12	15.0 x 3.0″	12.05	8.22	5.56	4.57	3.65	67.16
17	25	2.12	5.0 x 10.0″	11.55	7.55	5.19	4.44	3.45	68.10
18	31	2.63	5.0 x 10.0″	10.98	6.08	5.29	4.44	4.03	71.05
19	28	2.36	5.0 x 10.0″	10.74	6.82	5.10	4.31	3.75	68.57
20	27	2.29	5.0 x 10.0″	11.26	7.28	5.24	4.41	4.13	70.70
21	30	2.54	5.0 x 10.0″	11.23	6.82	5.02	4.28	3.89	69.17
22	28	2.37	5.0 x 10.0″	11.39	7.99	5.27	4.54	4.02	68.92
23	28	2.37	6.0 x 8.0″	11.76	8.27	5.47	4.60	4.08	69.17
24	27	2.29	6.0 x 8.0″	10.93	8.21	5.24	4.54	3.84	69.40
25	23	1.95	4.5 x 10.0″	11.24	8.74	5.62	4.80	3.93	67.63

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FINISHED BLACK CHROME-TANNED KIP LEATHER (Continued)

Section Number	Weight in grams	Per cent of total weight	Size of cutting	Moisture Per cent	Petrol fat Per cent	Ash Per cent	Chrome Per cent	Sulfates Per cent	Hide substance Per cent
26	22	1.86	4.5 x 10.0″	11.38	9.46	5.21	4.51	3.88	68.81
27	25	2.12	4.5 x 10.0″	11.74	7.81	5.57	4.73	3.93	68.81
28	21	1.78	4.5 x 10.0″	11.30	10.50	5.55	4.60	3.69	67.16
29	23	1.95	4.5 x 9.0″	11.24	7.82	5.32	4.67	3.84	68.10
30	21	1.78	4.5 x 9.0″	10.99	8.52	5.16	4.54	3.51	68.34
31	23	1.95	4.5 x 9.0″	11.77	6.88	5.26	4.38	4.09	68.93
32	23	1.95	4.5 x 9.0″	11.44	7.89	5.33	4.35	4.03	69.52
33	18	1.53	3.0 x 10.0″	11.54	6.30	5.29	4.64	3.89	70.11
34	18	1.53	3.0 x 10.0″	11.73	7.08	5.15	4.41	4.01	69.79
35	17	1.44	3.0 x 10.0″	11.14	6.03	5.34	4.48	3.80	70.93
36	17	1.44	3.0 x 10.0″	11.29	6.48	5.23	4.51	3.59	71.99
37	24	2.03	4.5 x 9.0″	11.97	7.62	5.30	4.51	3.89	68.57
38	25	2.12	4.5 x 9.0″	11.52	6.98	5.09	4.35	3.98	70.70
39	24	2.03	4.5 x 9.0″	11.88	7.40	5.17	4.35	3.77	70.11
40	27	2.29	4.5 x 9.0″	11.31	6.44	5.18	4.25	3.94	70.34
41	18	1.53	3.0 x 10.0″	11.61	6.67	5.21	4.31	3.99	69.05
42	20	1.69	3.0 x 10.0″	11.29	6.18	5.16	4.35	3.99	67.87
43	18	1.53	3.0 x 10.0″	11.14	6.12	5.26	4.31	3.61	69.64
44	18	1.53	3.0 x 10.0″	11.75	6.04	5.30	4.41	3.86	67.16
*x	58	4.92		10.43	11.71	5.72	4.67	3.83	60.55
Average					8.43	5.44	4.44	3.81	67.01

*x equals P. and V. method of sampling. Analysis calculated on 12 per cent. moisture basis.

AUG. C. ORTHMANN,
Chemist.

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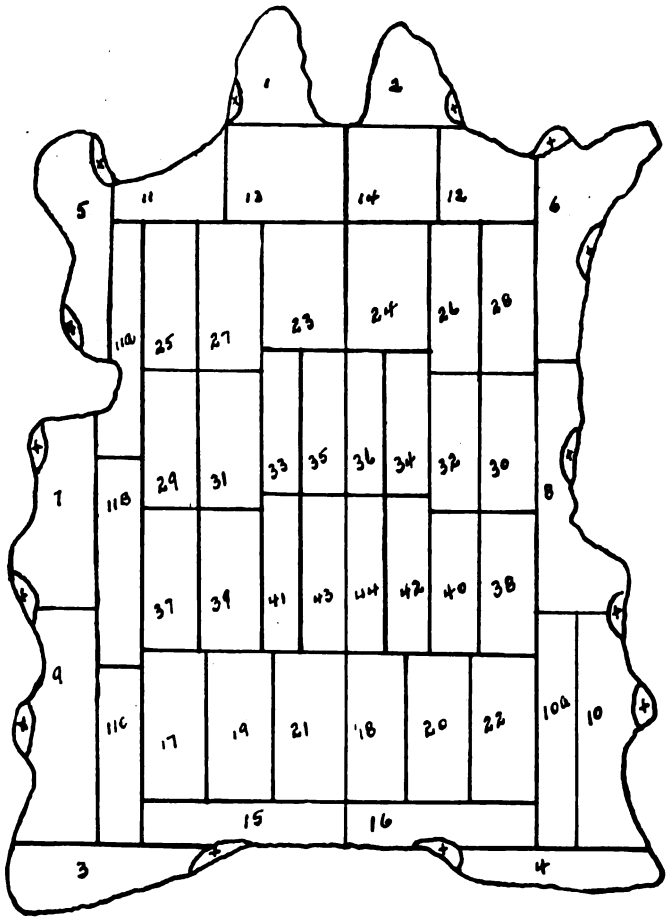

FINISHED BLACK CHROME-TANNED KIP

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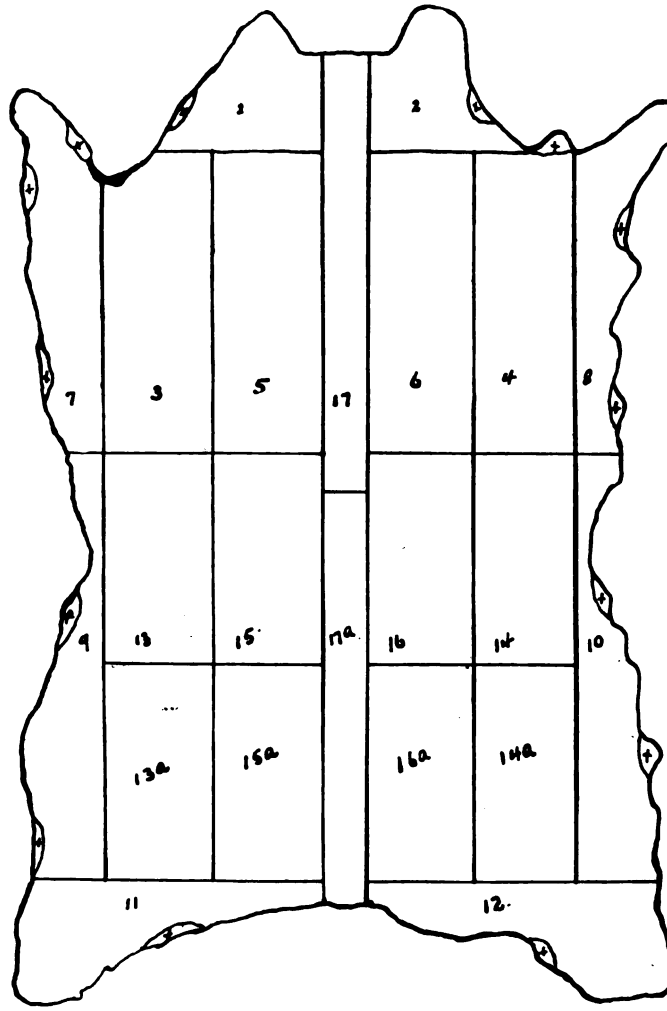

FINISHED CHROME—TANNED BLACK KID

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FINISHED CHROME-TANNED BLACK KID LEATHER

Section number	Weight in grams	Per cent of total weight	Size of cutting	Moisture Per cent	Petrol fat Per cent.	Ash Per cent.	Chrome Per cent.	Sulfates Per cent.	Hide substance Per cent.
1	20	5.10	9 x 8.5"	11.82	8.20	5.66	4.59	4.01	67.93
2	21	5.36	10 x 8.5"	11.93	8.33	5.73	4.57	3.85	67.28
3	18	4.59	5.25 x 9 x 10.0"	12.56	8.32	5.52	4.60	3.74	68.27
4	22	5.61	5.5 x 10 x 11.0"	12.61	8.67	5.60	4.63	3.38	66.81
5	21	5.36	5.25 x 10.0"	12.74	7.74	5.54	4.51	4.00	68.40
6	22	5.61	5.5 x 10.0"	12.37	7.67	5.51	4.55	3.82	68.40
7	17	4.34	3 x 9.0"	11.73	9.33	5.75	4.63	3.79	65.66
8	14	3.57	3 x 11.0"	11.36	8.69	5.91	4.70	3.51	65.38
9	16	4.08	3.25 x 15.0"	10.96	9.74	5.62	4.51	3.60	64.61
10	14	3.57	4.5 x 15.0"	11.59	9.48	5.83	4.58	3.78	64.58
11	20	5.10	14 x 1.0"	11.67	11.17	5.65	4.46	3.48	64.15
12	19	4.85	15 x 1.0"	12.05	9.87	5.76	4.71	3.69	65.91
13	15	3.83	5.25 x 7.5"	12.10	7.99	5.55	4.60	3.13	71.35
13 a	15	3.83	5.25 x 7.5"	11.90	8.20	5.53	4.57	3.92	70.20
14	15	3.83	5.5 x 7.5"	10.89	7.90	5.62	4.58	3.13	70.82
14 a	13	3.32	5.5 x 7.5"	11.97	8.25	5.67	4.60	3.92	70.26
15	16	4.08	5.25 x 7.5"	12.26	7.95	5.68	4.66	3.92	67.54
15 a	16	4.08	5.25 x 7.5"	11.78	7.70	5.54	4.50	3.89	67.66
16	16	4.08	5.5 x 7.5"	12.21	7.73	5.46	4.61	3.86	67.50
16 a	16	4.08	5.5 x 7.5"	12.15	7.70	5.55	4.65	4.07	67.94
17	15	3.83	2.0 x 17.5"	11.61	7.97	5.42	4.42	3.62	67.04
17 a	16	4.08	2.0 x 17.5"	11.68	7.81	5.65	4.55	3.92	67.58
*x	15	3.83		11.53	10.28	5.69	4.51	4.11	66.99
Average					8.56	5.73	4.58	3.75	68.46

*x equals P. and V. method of sampling. Analysis calculated on 12 per cent. moisture basis.

AUG. C. ORTHMANN,
Chemist.

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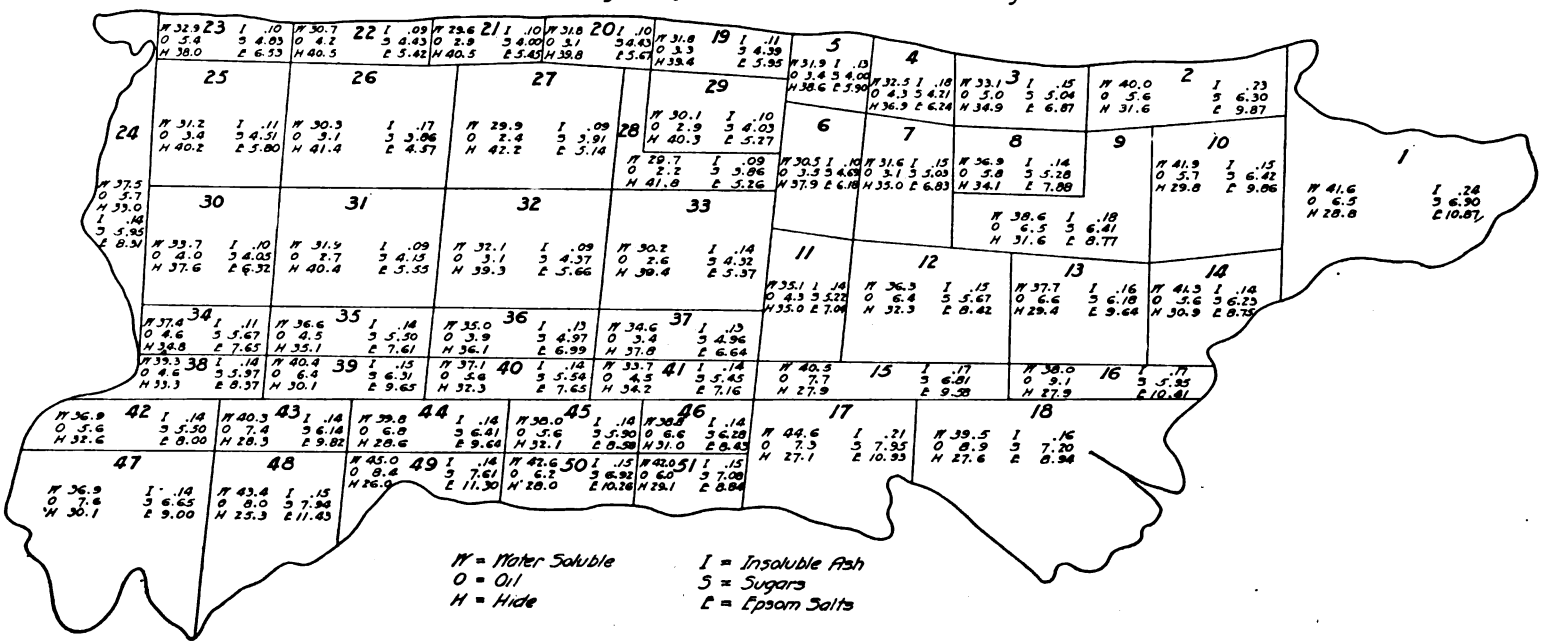
Figure 1

Side of Heavy Slaughter Leather. Alsop - Elk Tanning Co.



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AVE. ANALYSIS OF THE VARIOUS CUTS ON BASIS OF LEATHER CONTAINING 13% MOISTURE (Figure 1)

	Wt. in grams	% of total wt.	Approx. surface area sq. in.	Oil and grease Petroleum ether ext.	Ash.	Epsom salts	Sugars	Water Solubles Non-tannin	Water Solubles Tannin	Hide substance
Side No. 1 to 51	10329.0	100.00	3475.7	4.45	2.90	6.68	4.81	17.58	13.79	29.74
Back and Head, Union No. 1 to 16 and 19 to 41	7910.5	76.58	2519.0	3.82	2.68	6.15	4.43	16.54	13.67	31.26
Back and Head, Oak, No. 1 to 14 and 19 to 37	7341.5	71.07	2301.0	3.69	2.63	6.03	4.37	16.33	13.64	31.59
Back, Union, No. 2 to 16 and 19 to 41	7345.5	71.11	2334.0	3.68	2.58	5.89	4.31	16.15	13.60	31.74
Back, Oak, No. 2 to 14 and 19 to 37	6776.5	65.60	2116.0	3.52	2.52	5.74	4.23	15.90	13.55	32.14
Bend, Union, No. 19 to 41	4736.0	45.85	1366.9	3.04	2.23	5.11	3.93	14.81	13.29	33.70
Bend, Oak, No. 19 to 37	4368.0	42.29	1239.4	2.91	2.16	4.93	3.84	15.50	12.41	34.15
Shoulder, Union No. 2 to 16	2609.5	25.26	967.1	4.84	3.21	7.32	5.00	18.60	13.80	28.18
Shoulder, Oak, No. 2 to 14	2408.5	23.31	876.6	4.63	3.17	7.21	4.95	18.44	13.82	28.50
Belly, Union, No. 17-18 and 42 to 51	2418.5	23.42	956.7	6.50	3.60	8.50	6.07	20.98	14.15	24.76
Belly, Oak, No. 15 to 18 and 38 to 51	2987.5	28.93	1174.7	6.32	3.55	8.35	5.91	20.62	14.15	25.17
Head No. 1	565.0	5.47	185.0	5.66	3.93	9.45	6.00	21.52	14.66	25.04

AVERAGE ANALYSIS OF THE VARIOUS CUTS ON BASIS OF MOISTURE FREE LEATHER

	Water Solubles Non-tannin	Water Solubles Tannin	Oil and grease Petroleum ether ext.	Hide Substance	Insoluble ash	Sugars	Epsom salts
Side No. 1 to 51	20.21	15.85	5.11	34.18	0.14	5.53	7.70
Back and Head, Union, No. 1 to 16 and 19 to 41	19.01	15.71	4.39	35.93	0.14	5.10	7.06
Back and Head, Oak, No. 1 to 14 and 19 to 37	18.74	15.71	4.24	36.31	0.14	5.02	6.93
Back, Union, No. 2 to 16 and 19 to 41	18.56	15.64	4.23	36.48	0.13	4.95	6.77
Back, Oak, No. 2 to 14 and 19 to 37	18.28	15.57	4.05	36.94	0.13	4.86	6.60
Bend, Union, No. 19 to 41	17.02	15.28	3.49	38.74	0.12	4.52	5.87
Bend, Oak, No. 19 to 37	17.82	14.26	3.34	39.25	0.12	4.41	5.67
Shoulder, Union, No. 2 to 16	21.38	15.86	5.56	32.39	0.16	5.75	8.41
Shoulder, Oak, No. 2 to 14	21.20	15.88	5.32	32.76	0.16	5.69	8.28
Belly, Union, No. 17-18 and 42 to 51	24.12	16.26	7.47	28.46	0.15	6.98	9.77
Belly, Oak, No. 15 to 18 and 38 to 51	23.70	16.27	7.26	28.93	0.15	6.80	9.60
Head No. 1	24.74	16.85	6.51	28.78	0.24	6.90	10.87

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ANALYSES OF 51 SAMPLES OF LEATHER (NOS. 1 TO 51) SECURED WHEN SIDE OF LEATHER WAS CUT (FIGURE 1.)

Sample No.	Weight grams	Per cent of weight	Approx. surface Sq. in.	Moisture	Oil and grease Pet. ether ext.	Ash	Epsom salts	Sugars	Water Solubles Non-tannin	Water Solubles Tannin	Hide substance
1	565	5.47	185	13.00	5.66	3.93	9.45	6.00	21.52	14.66	25.04
2	203.5	1.97	65	13.00	4.83	3.55	8.58	5.48	19.85	14.94	27.46
3	138.5	1.34	51.2	13.00	4.32	2.73	5.97	4.38	15.85	12.91	30.38
4	86	.83	32	13.00	3.70	2.43	5.43	3.66	15.06	13.18	32.14
5	90.5	.88	32.5	13.00	2.92	2.13	5.13	3.48	14.48	13.29	33.54
6	158	1.53	63.3	13.00	3.05	2.31	5.37	4.08	14.55	11.99	32.96
7	143	1.38	63.5	13.00	2.72	2.62	5.94	4.37	15.54	11.92	30.46
8	119.5	1.16	50	13.00	5.00	3.00	6.85	4.59	17.62	14.45	29.65
9	185	1.79	72.9	13.00	5.65	3.47	7.63	5.57	19.29	14.25	27.49
10	311	3.01	100	13.00	4.94	3.75	8.57	5.58	21.33	15.14	25.95
11	176	1.70	61.8	13.00	3.70	2.68	6.12	4.54	17.20	13.37	30.44
12	253	2.45	106.4	13.00	5.54	3.09	7.32	4.93	18.34	13.27	28.07
13	242	2.34	97	13.00	5.78	3.64	8.38	5.37	19.85	12.98	25.61
14	302.5	2.93	81	13.00	4.90	3.61	7.61	5.42	20.72	15.22	26.89
15	98	.95	47.5	13.00	6.73	3.64	8.33	5.92	20.94	14.30	24.24
16	103	1.00	43	13.00	7.91	3.82	9.05	5.17	20.04	13.04	24.29
17	267.5	2.59	114	13.00	6.33	4.27	9.50	6.91	22.35	16.44	23.58
18	406	3.93	190	13.00	7.75	4.23	7.77	6.26	21.66	12.72	24.05
19	110	1.06	35	13.00	2.85	2.19	5.17	3.82	14.50	13.18	34.28
20	89.5	.87	28.9	13.00	2.69	2.12	4.93	3.85	14.26	13.44	34.64
21	88	.85	29.7	13.00	2.56	2.00	4.74	3.48	13.50	12.26	35.25
22	116	1.12	37	13.00	3.67	1.97	4.71	3.85	13.86	12.86	35.22
23	114	1.10	35	13.00	4.72	2.27	5.68	4.20	15.51	13.12	33.02
24	255	2.47	90	13.00	4.93	3.11	7.23	5.17	18.30	14.34	28.67
25	316	3.06	95	13.00	2.95	2.08	5.04	3.92	14.26	12.89	34.94
26	426	4.12	124.3	13.00	2.68	1.80	3.97	3.36	12.76	13.56	36.95

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ANALYSES OF 51 SAMPLES OF LEATHER (NOS. 1 TO 51) SECURED WHEN SIDE OF LEATHER WAS CUT (FIGURE 1.) (Continued)

Sample No.	Weight grams	Per cent of weight	Approx. surface Sq. in	Moisture	Oil and grease Pet. ether ext.	Ash	Epsom salts	Sugars	Water Solubles Non-tannin	Water Solubles Tannin	Hide substance
27	424	4.11	121.1	13.00	2.05	1.88	4.47	3.40	13.33	12.66	36.67
28	146	1.41	43.6	13.00	1.95	1.88	4.58	3.36	13.19	12.68	36.36
29	187	1.81	65	13.00	2.53	1.94	4.59	3.50	13.29	12.92	35.10
30	327	3.17	92.6	13.00	3.44	2.35	5.50	3.52	15.51	13.79	32.73
31	458	4.43	124.3	13.00	2.33	1.95	4.83	3.61	13.78	13.93	35.17
32	443	4.29	49.7	13.00	2.71	2.06	4.92	3.80	14.20	13.74	34.17
33	359	3.48	113.3	13.00	2.29	2.03	4.67	3.76	13.98	12.27	34.29
34	109	1.06	32.3	13.00	3.96	2.87	6.65	4.93	17.68	14.82	30.29
35	143	1.38	43	13.00	3.88	2.83	6.62	4.78	17.27	14.53	30.57
36	139	1.35	40.6	13.00	3.37	2.58	6.08	4.32	16.38	14.05	31.41
37	118.5	1.15	39	13.00	2.94	2.49	5.77	4.31	15.91	14.06	32.89
38	98.5	.95	31	13.00	4.02	3.13	7.28	5.19	18.95	15.20	28.95
39	93.5	.90	34	13.00	5.56	3.76	8.39	5.49	20.45	14.66	26.22
40	94	.91	32.5	13.00	4.88	2.92	6.65	4.82	17.59	14.73	28.96
41	82	.80	30	13.00	3.89	2.77	6.23	4.74	16.51	12.79	29.76
42	148.5	1.44	47	13.00	4.88	3.13	6.96	4.78	17.98	14.13	28.36
43	107	1.04	40.5	13.00	6.40	3.87	8.54	5.34	20.53	14.54	24.62
44	120	1.16	50	13.00	5.88	3.72	8.38	5.57	20.80	13.78	24.91
45	105	1.02	40	13.00	4.84	3.15	7.46	5.13	18.57	14.47	27.89
46	83	.80	32	13.00	5.72	3.18	7.33	5.46	19.08	14.69	26.95
47	522.5	5.06	204	13.00	6.62	3.39	7.83	5.78	19.39	12.69	26.14
48	295.5	2.86	100	13.00	6.97	2.51	9.94	6.90	23.36	14.42	21.99
49	166	1.61	64.7	13.00	7.30	4.23	9.83	6.61	23.56	15.55	22.61
50	114.5	1.11	42.5	13.00	5.40	3.72	8.92	6.02	21.63	15.45	24.39
51	83	.80	32	13.00	5.20	3.54	7.69	6.16	20.85	15.65	25.34
Av.	10329	100.00	3475.7	13.00	4.45	2.90	6.68	4.81	17.58	13.79	29.74

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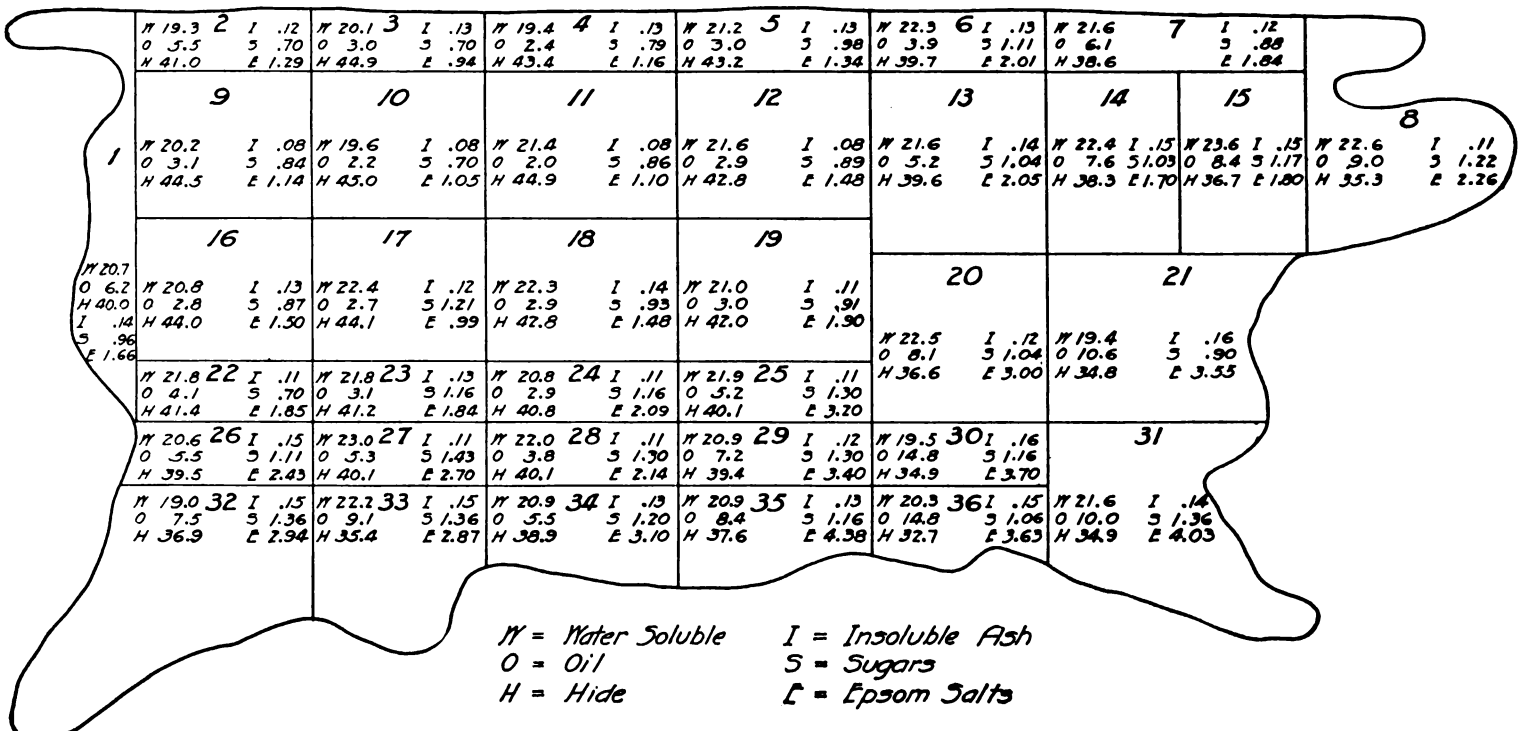
Figure 2

Side of Rough Belting Leather. Rogers-Kistler, Lesh and Co.



W = Water Soluble I = Insoluble Ash
O = Oil S = Sugars
H = Hide L = Epsom Salts

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AVERAGE OF THE VARIOUS CUTS ON BASIS OF MOISTURE FREE LEATHER (FIGURE 2)

	Water Solubles						
	Non-tannin	Tannin	Oil and grease Pet. ether ext.	Hide substance	Insol. ash	Sugars	Epsom salts
Side, No. 1-36	7.90	13.30	5.90	39.58	.13	1.06	2.16
Back, No. 1-25	7.64	13.79	5.01	40.60	.12	.98	1.77
Butt, No. 1-7, 9-25	7.58	13.69	4.48	41.31	.12	.95	1.71
Bend, No. 1-5, 9-12, 16-19, 22-25	7.30	13.71	3.25	42.97	.11	.92	1.45
Belly, No. 26-36	8.60	11.98	8.31	36.81	.14	1.29	3.22
Whole Shoulder, No. 6-8, 13-15, 20-21	8.20	13.91	7.86	36.77	.13	1.08	2.30
Trim Shoulder, No. 6-7, 13-15, 20-21	8.24	13.65	7.38	37.43	.14	1.02	2.32
Head, No. 8	8.09	14.51	8.97	35.28	.12	1.22	2.25

AVERAGE ANALYSIS OF THE VARIOUS CUTS ON BASIS OF THE ORIGINAL LEATHER

	Weight in grams	Per cent. of total weight	Approx. surface area Sq. in.	Mois-ture	Oil and grease Pet. ether ext.	Ash	Epsom salts	Sugars	Water Solubles Non-tannins	Tannin	Hide sub-stance
Side, No. 1-36	9259	100.00	3128	12.86	5.27	.87	1.89	.93	6.89	11.59	34.49
Back, No. 1-25	6774	73.17	2134	13.25	4.52	.78	1.54	.85	6.63	11.97	35.22
Butt, No. 1-7, 9-25	5979	64.58	1894	13.27	4.08	.77	1.48	.82	6.58	11.88	35.83
Bend, No. 1-5, 9-12, 16-19, 22-25	4190	45.27	1248	13.59	3.07	.68	1.25	.79	6.31	11.86	37.14
Belly, No. 26-36	2485	26.83	994	11.79	7.33	1.09	2.85	1.13	7.59	10.57	32.51
Whole Shoulder, No. 6-8, 13-15, 20-21	2584	27.90	886	12.71	6.87	.95	2.01	.95	7.15	12.15	32.10
Trim Shoulder, No. 6-7, 13-15, 20-21	1789	19.31	646	12.54	6.45	.98	2.03	.90	7.21	11.94	32.74
Head, No. 8	795	8.59	240	13.07	7.80	.89	1.96	1.06	7.03	12.61	30.67

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Analyses of Samples on Basis of the Original Leather (figure 2.)

Sample No.	Weight in grams	Per cent of total weight	Approx. surface area Sq. in.	Mois ture	Oil and grease Petroleum ether ext.	Ash	Epsom salts	Sugars	Water Solubles Non-tannin	Water Solubles Tannin	Hide substance
1	310	3.35	96	13.68	5.31	1.41	1.43	0.83	6.75	11.13	34.49
2	169	1.82	48	13.95	4.74	0.87	1.11	0.60	5.75	10.84	35.29
3	154	1.67	48	14.08	2.54	0.69	0.81	0.60	5.97	11.33	38.59
4	146	1.58	48	13.67	2.09	0.82	1.00	0.68	5.97	10.82	37.42
5	137	1.48	48	13.56	2.60	0.92	1.16	0.85	6.32	12.04	37.30
6	142	1.53	48	13.42	3.39	1.17	1.74	0.96	7.13	12.20	34.38
7	227	2.45	68	13.36	5.26	0.38	1.59	0.76	6.34	12.34	33.48
8	795	8.59	240	13.07	7.80	0.89	1.96	1.06	7.03	12.61	30.67
9	341	3.68	96	13.87	2.64	0.41	0.98	0.72	5.72	11.71	38.31
10	347	3.75	96	14.31	1.92	0.40	0.90	0.60	5.86	10.96	38.54
11	333	3.60	96	13.73	1.76	0.40	0.94	0.74	5.95	12.52	38.71
12	298	3.22	96	13.59	2.49	0.35	1.28	0.77	6.22	12.46	36.99
13	321	3.47	120	13.10	4.49	1.07	1.78	0.90	7.03	11.73	34.38
14	230	2.48	85	12.96	6.65	1.06	1.47	0.90	7.10	12.38	32.36
15	304	3.28	85	13.02	7.29	1.13	1.56	1.02	7.52	13.03	31.91
16	340	3.67	96	14.68	2.41	0.80	1.27	0.74	5.95	11.81	37.53
17	379	4.10	96	13.91	2.32	0.70	0.85	1.04	6.59	12.67	37.98
18	349	3.77	96	13.85	2.46	0.68	1.28	0.80	6.44	12.74	36.85
19	297	3.21	96	12.46	2.58	0.88	1.66	0.80	6.85	11.51	36.74
20	287	3.10	120	11.36	7.15	0.86	2.65	0.92	7.35	12.57	32.47
21	278	3.00	120	11.13	9.44	1.18	3.16	0.80	7.78	9.50	30.90
22	159	1.72	48	12.50	3.57	0.57	1.62	0.60	6.24	12.86	36.18
23	160	1.73	48	12.36	2.75	0.58	1.61	1.02	7.17	11.95	36.07
24	144	1.55	48	11.84	2.51	0.57	1.84	1.02	7.04	11.26	35.95
25	127	1.37	48	11.97	4.61	0.77	2.81	1.14	7.45	11.80	35.31
26	143	1.54	48	11.92	4.85	0.63	2.14	0.98	6.50	11.68	34.77
27	105	1.13	48	11.62	4.71	0.70	2.38	1.26	7.46	12.87	35.45
28	128	1.38	48	11.69	3.34	0.57	1.89	1.14	7.37	12.04	35.39
29	111	1.20	48	11.79	6.37	0.75	3.00	1.14	7.13	11.32	34.77
30	97	1.05	48	14.02	12.76	0.69	3.19	1.00	7.11	9.69	29.97
31	344	3.71	140	11.67	8.87	1.20	3.56	1.20	8.54	10.56	30.84
32	765	8.26	230	11.47	6.61	1.18	2.60	1.20	7.43	9.38	32.64
33	247	2.67	96	11.56	8.08	1.35	2.54	1.20	8.00	11.63	31.29
34	182	1.97	96	12.53	4.84	1.15	2.71	1.04	7.45	10.80	33.99
35	191	2.06	96	12.24	7.37	1.28	3.85	1.02	7.44	10.92	32.98
36	172	1.86	96	11.27	13.16	1.28	3.22	0.94	7.80	10.26	29.04
Average				12.86	5.27	0.87	1.89	0.93	6.89	11.59	34.49

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Analyses of Samples on Basis of the Original Leather (see figure 3)

Sample No.	Weight in grams	Per cent. of total weight	Moisture	Oil and grease Petroleum ether ext.	Ash	Water Solubles: Epsom salts	Sugars	Non-tannin	Tannin	Hide substance
1	302	2.62	9.65	2.32	1.56	4.62	4.98	14.30	13.02	35.46
2	223	1.94	10.28	1.64	1.46	5.32	4.79	13.06	11.83	37.28
3	226	1.96	9.79	1.30	1.32	4.10	4.00	12.55	11.29	38.06
4	221	1.92	10.35	1.60	1.37	3.75	4.28	12.16	12.38	36.44
5	224	1.94	10.72	1.47	1.53	4.45	5.17	12.80	12.15	35.70
6	220	1.91	10.89	1.33	1.46	4.49	5.16	12.87	12.89	35.36
7	320	2.78	10.13	2.10	1.50	3.96	5.68	13.31	11.89	33.93
8	563	4.89	10.83	3.64	1.94	3.72	6.08	14.70	15.65	30.98
9	460	3.99	8.10	1.33	1.28	3.94	4.26	12.92	11.76	40.37
10	461	4.00	9.06	1.15	1.24	4.31	3.99	12.19	11.32	40.33
11	440	3.82	11.41	1.14	1.30	4.15	4.27	12.17	12.03	35.90
12	442	3.84	10.81	1.21	1.28	3.14	3.62	11.31	11.31	36.83
13	460	3.99	11.06	1.26	1.34	3.15	4.90	12.46	12.91	34.67
14	330	2.87	10.32	2.43	1.64	3.00	5.92	13.49	12.52	33.49
15	340	2.95	10.54	2.41	1.64	3.73	6.11	13.80	14.41	32.32
16	450	3.91	8.95	1.24	1.26	4.01	3.62	12.32	12.22	37.28
17	451	3.92	9.10	1.07	1.26	4.44	3.82	12.41	12.12	37.97
18	437	3.79	9.12	1.34	1.41	4.33	4.39	12.91	13.28	35.36
19	435	3.78	10.33	0.78	1.35	4.12	4.51	12.94	12.85	36.15
20	420	3.65	10.65	1.14	1.46	3.84	4.70	12.87	12.82	31.28
21	465	4.04	9.52	2.72	1.88	6.33	5.94	14.88	14.79	31.97
22	153	1.33	9.17	1.32	1.44	4.66	3.98	12.89	13.15	36.25
23	150	1.30	9.28	1.09	1.52	5.18	4.14	13.65	13.79	35.12
24	130	1.13	12.81	1.00	1.52	4.95	5.38	13.30	12.45	33.10
25	146	1.27	10.51	1.06	1.53	4.52	6.03	14.67	13.54	34.04
26	143	1.24	10.37	2.31	1.56	5.04	4.15	13.08	13.36	33.11
27	128	1.11	8.95	2.34	1.76	6.08	4.30	14.18	14.05	32.55
28	118	1.02	9.10	1.40	1.67	4.81	6.17	15.20	13.47	33.62
29	130	1.13	10.47	0.85	1.40	4.08	5.34	13.49	12.90	34.72
30	141	1.22	11.18	2.44	2.16	6.15	5.42	15.84	14.51	30.30
31	495	4.30	10.10	3.90	2.15	7.12	6.87	15.97	13.71	29.80
32	719	6.24	9.33	3.46	1.82	5.84	5.73	14.86	13.89	31.38
33	330	2.87	8.96	3.57	2.25	6.63	6.14	16.64	14.52	29.17
34	285	2.47	8.40	3.02	2.09	6.44	6.54	17.74	13.59	30.88
35	290	2.52	9.93	1.70	1.83	5.11	6.20	15.69	14.03	31.62
36	270	2.34	10.81	2.83	2.69	7.65	6.81	16.42	14.25	28.43
Average			9.93	2.00	1.60	4.70	5.10	13.72	13.10	34.20

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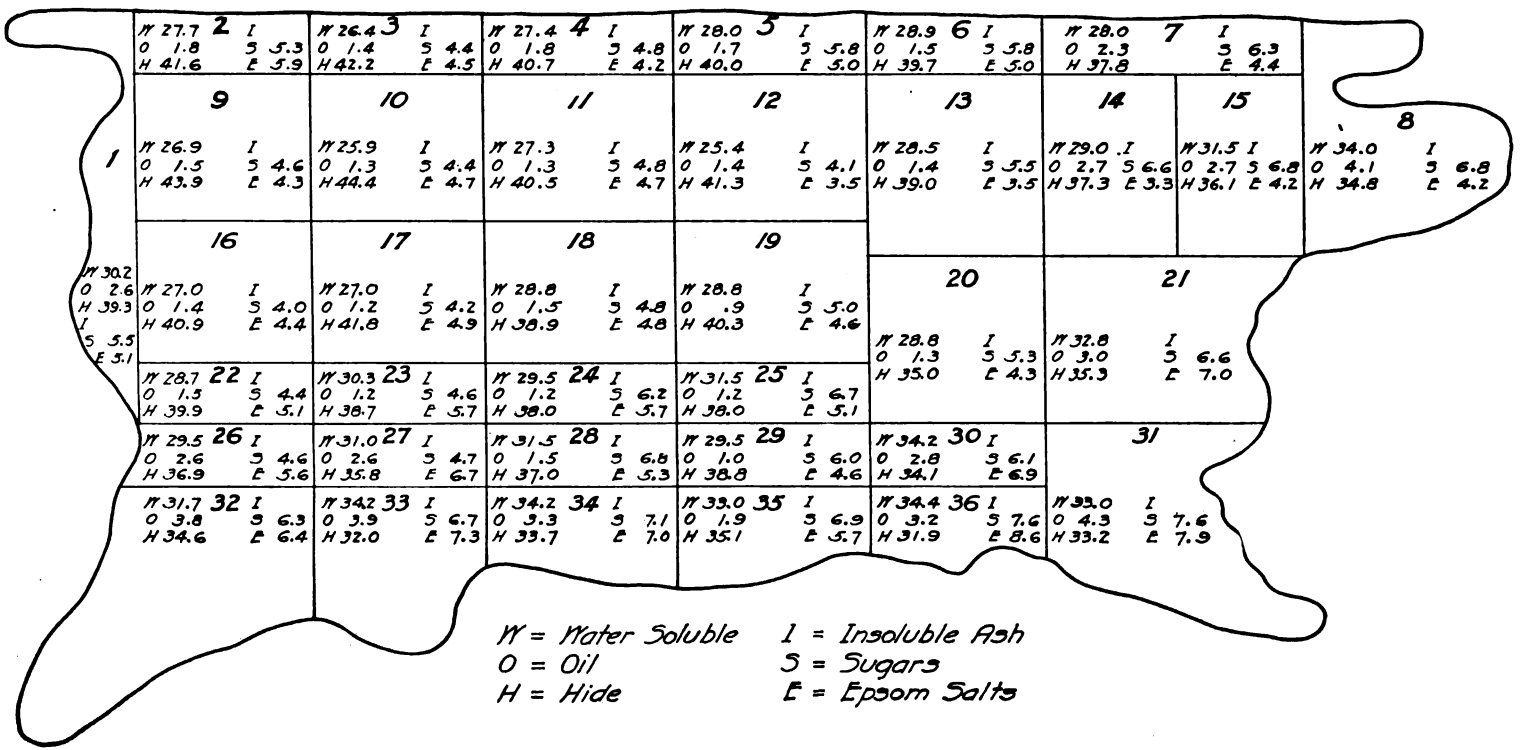
Figure 3

Side of Heavy Union Sole Leather. Seltzer - Kistler Leather Co.



W = Water Soluble I = Insoluble Ash
O = Oil S = Sugars
H = Hide E = Epsom Salts

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AVERAGE ANALYSIS OF THE VARIOUS CUTS ON BASIS OF THE ORIGINAL LEATHER (FIGURE 3)

	Weight in grams	Per cent. of total weight	Moisture	Oil and grease Petroleum ether ext.	Ash	Epsom salts	Sugars	Water Solubles Non-tannin	Water Solubles Tannin	Hide substance
Side, No. 1 to 36	11518		9.93	1.99	1.60	4.71	5.10	13.72	13.09	34.19
Back, No. 1 to 25	8469	73.52	10.02	1.63	1.47	4.22	4.78	13.06	12.80	35.39
Butt, No. 1 to 7 and 9 to 25	7906	68.64	9.98	1.49	1.43	4.25	4.66	12.90	12.59	35.72
Bend, No. 1 to 5, 9 to 12, 16 to 19 and 22 to 25	5351	46.46	9.79	1.28	1.35	4.22	4.28	12.80	12.27	36.95
Belly, No. 26 to 36	3049	26.48	9.68	2.94	1.97	6.10	6.03	15.60	13.90	30.91
Whole Shoulder, No. 6 to 8, 13 to 16, and 20-21	3118	27.06	10.43	2.23	1.67	4.18	5.58	13.66	13.70	32.72
Trimmed Shoulder, No. 6-7, 13 to 15 and 20-21	2555	22.18	10.33	1.92	1.61	4.32	5.47	13.43	13.27	33.11
Head, No. 8	563	4.88	10.83	3.64	1.94	3.72	6.08	14.70	15.65	30.98

AVERAGE ANALYSIS OF THE VARIOUS CUTS ON BASIS OF MOISTURE FREE LEATHER (FIGURE 3)

	Water Solubles Non-tannin	Water Solubles Tannin	Oil and grease Pet. ether ext.	Hide substance	Sugars	Epsom salts
Side, No. 1 to 36	15.24	14.53	2.21	37.96	5.66	5.23
Back, No. 1 to 25	14.51	14.22	1.81	39.33	5.31	4.69
Butt, No. 1 to 7 and 9 to 25	14.37	13.98	1.66	39.65	5.18	4.72
Bend, No. 1 to 5, 9 to 12, 16 to 19 and 22 to 25	14.07	13.60	1.42	40.96	4.74	4.68
Belly, No. 26 to 36	17.27	15.39	3.25	34.22	6.68	6.75
Whole Shoulder, No. 6 to 8, 13 to 15 and 20-21	15.25	15.29	2.49	36.54	6.23	4.67
Trimmed Shoulder, No. 6-7, 13 to 15 and 20-21	14.98	14.80	2.14	36.92	6.10	4.82
Head, No. 8	16.49	17.55	4.08	34.78	6.82	4.17

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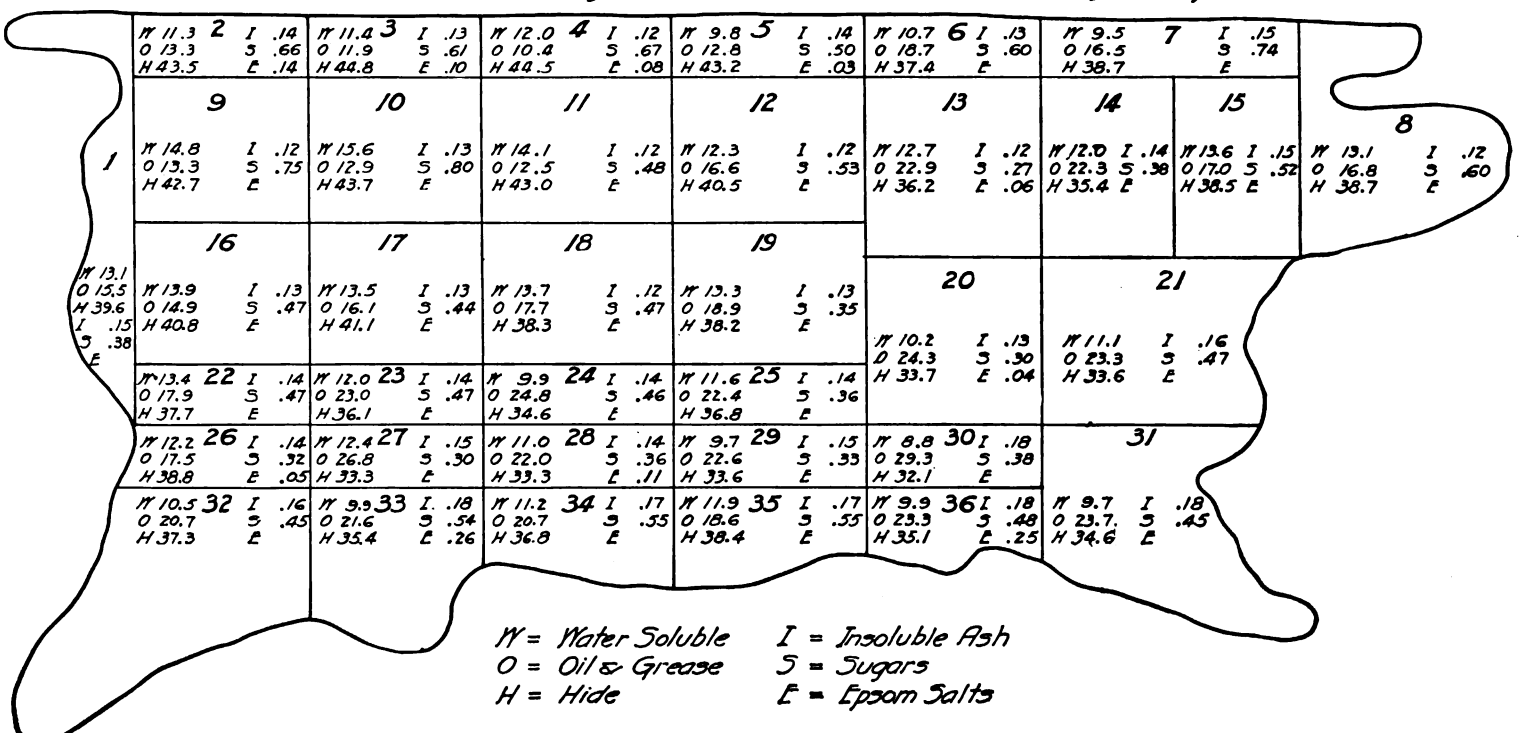
Figure 4

Side of Curried Belting Leather. Small-Graton & Knight Mfg. Co.



W = Water Soluble I = Insoluble Ash
O = Oil & Grease S = Sugars
H = Hide E = Epsom Salts

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AVERAGE ANALYSIS OF THE VARIOUS CUTS ON BASIS OF THE ORIGINAL LEATHER (FIGURE 4)

	Weight in grams	Per cent. of total weight	Approx. surface area Sq. in	Moisture	Oil and grease Pet. ether ext.	Ash	Sugars	Water Solubles Non-tannin	Tannin	Hide substance
Side, No. 1 to 36	7989.9	100.00	3355	7.28	17.00	.25	.46	2.35	8.92	34.64
Back, No. 1 to 25	5825.9	72.91	2176	7.67	15.83	.24	.50	2.45	9.36	36.39
Butt, No. 1 to 7 and 9 to 25	5460.9	68.34	1998	7.70	15.85	.24	.49	2.45	9.34	36.44
Bend, No. 1-5, 9 to 12, 16 to 19 and 22 to 25	3863.8	48.36	1329	8.15	14.29	.23	.52	2.56	9.69	37.67
Belly, No. 26 to 36	2164.0	27.08	1179	6.24	20.28	.30	.41	2.05	7.86	33.78
Whole Shoulder, No. 6 to 8, 13 to 15 and 20 to 21	1962.1	24.56	847	6.74	18.87	.25	.44	2.27	8.70	34.10
Trimmed Shoulder, No. 6 to 7, 13 to 15 and 20-21	1597.1	20.00	669	6.62	19.62	.25	.42	2.20	8.48	33.69
Head, No. 8	365.0	4.56	176	7.25	15.59	.21	.56	2.58	9.58	35.88

AVERAGE ANALYSIS OF THE VARIOUS CUTS ON BASIS OF MOISTURE FREE LEATHER

	Water Solubles Non-tannin	Tannin	Oil and grease Pet. ether ext.	Hide substance	Insoluble ash	Sugars
Side, No. 1 to 36	2.54	9.62	18.34	38.45	.15	.49
Back, No. 1 to 25	2.66	10.14	17.15	39.43	.14	.54
Butt, No. 1 to 7 and 9 to 25	2.66	10.12	17.17	39.48	.14	.53
Bend, No. 1 to 5, 9 to 12, 16 to 19 and 22 to 25	2.79	10.56	15.57	40.93	.14	.56
Belly, No. 26 to 36	2.19	8.38	21.64	36.01	.17	.44
Whole Shoulder, No. 6 to 8, 13 to 15 and 20-21	2.43	9.32	20.23	36.55	.15	.47
Trimmed Shoulder, No. 6-7, 13 to 15 and 20-21	2.36	9.08	21.01	36.07	.15	.45
Head, No. 8	2.78	10.33	16.82	38.71	.12	.60

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Analysis of Samples on Basis of the Original Leather (see figure 4)

No. sample	Weight in grams	Per cent of total weight	Approx. surface area Sq. in.	Moisture	Oil and grease Petroleum ether ext.	Ash	Epsom salts	Water Solubles: Sugars	Water Solubles: Non-tannin	Water Solubles: Tannin	Hide substance	Character of leather
1	192.8	2.41	83	6.37	14.55	.28		.36	2.45	9.78	37.06	Fairly firm—lower right soft.
2	118.0	1.48	43	7.02	12.40	.23	.13	.62	2.53	7.83	40.40	Fairly firm—except lower right hand corner.
3	130.8	1.65	44	7.03	11.07	.23	.08	.57	2.54	8.06	41.67	Good throughout.
4	128.2	1.61	44	7.50	9.62	.27	.07	.62	2.48	8.62	41.17	Good throughout.
5	104.2	1.30	40	7.68	11.78	.25	.03	.45	1.96	7.13	39.91	Good throughout.
6	91.5	1.14	40	6.24	17.57	.23		.56	2.08	7.90	35.03	Little soft.
7	247.7	3.10	106	4.95	15.72	.27		.70	2.33	6.68	36.81	Firm at top. Soft at bottom.
8	365.0	4.56	176	7.25	15.60	.21		.56	2.58	9.58	35.90	Firm at bottom—flanky at top.
9	365.7	4.57	117	8.92	12.15	.22		.68	2.89	10.86	38.88	Soft in left hnd. cor. rest firm.
10	368.3	4.60	115	9.03	11.78	.23		.72	3.05	11.14	39.77	Good throughout.
11	364.8	4.56	114	9.11	11.35	.21		.44	2.79	10.06	39.10	Good throughout.
12	319.0	3.99	115	8.73	15.16	.21		.48	2.40	8.86	36.92	Little soft at top. Rest firm.
13	299.8	3.75	138	7.63	21.17	.22	.06	.25	2.27	9.46	33.40	Good texture, but thinner.
14	207.8	2.60	101	7.49	20.61	.25		.35	2.17	8.88	32.73	Good texture, but thinner.
15	239.0	2.99	104	8.00	15.62	.27		.48	2.61	9.91	35.40	Little heavier at top. Good texture.
16	341.0	4.26	114	8.55	13.61	.23		.43	2.63	10.07	37.33	Soft in left hnd. cor. Rest firm.
17	387.2	4.84	114	8.50	14.74	.23		.40	2.49	9.88	37.63	Good throughout.
18	349.2	4.37	115	8.04	16.25	.22		.43	2.46	10.12	35.23	Little soft in lower right hnd. cor. Rest good.
19	313.4	3.92	114	7.92	17.44	.23		.32	2.41	9.79	35.19	Little soft in upper right hnd. cor.
20	266.0	3.33	134	5.90	22.86	.24	.04	.28	1.78	7.80	31.70	Much thinner, soft on right side.
21	245.3	3.07	143	5.87	21.95	.29		.44	2.10	8.31	31.65	Firm on left side. Flanky on right.

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ANALYSIS OF SAMPLES ON BASIS OF THE ORIGINAL LEATHER. (FIGURE 4) (Continued)

No. sample	Weight in grams	Per cent of total weight	Approx. surface area Sq. in.	Moisture	Oil and grease Petroleum ether ext.	Ash	Epsom salts	Water Solubles: Sugars	Water Solubles: Non-tannin	Water Solubles: Tannin	Hide substance	Character of leather
22	98.2	1.23	38	7.17	16.63	.25		.44	2.47	9.97	34.96	Little soft at bottom, but fairly firm.
23	96.4	1.21	38	6.70	21.48	.25		.44	2.14	9.08	33.63	Somewhat flanky. Good texture.
24	99.0	1.24	37	6.45	23.18	.25		.43	2.03	7.19	32.33	Somewhat flanky. Good texture.
25	87.6	1.10	37	6.50	20.95	.25		.34	2.19	8.61	34.42	Somewhat flanky. Good texture.
26	108.2	1.38	51	6.84	16.30	.26	.05	.30	2.55	8.85	36.15	Good texture.
27	73.2	0.92	39	5.78	25.28	.27		.28	2.48	9.17	31.34	Very pipey except on lower left.
28	95.0	1.20	40	6.81	20.50	.25	.10	.34	2.07	8.21	31.00	Somewhat flanky. Good texture.
29	84.1	1.06	39	6.41	21.16	.28		.31	1.48	7.63	31.44	Flanky at top, firm at bottom.
30	61.5	0.77	40	5.25	27.77	.32		.36	1.76	6.58	30.38	Flanky at top and bottom. Firm in middle.
31	299.0	3.74	210	5.72	22.34	.33		.42	1.97	7.13	32.58	Soft, thin and flanky throughout.
32 a	349.6	4.37	171	6.14	20.58	.27		.38	1.91	7.50	34.55	Top spongy. Rest firm.
32 b	288.0	3.60	154	6.13	18.04	.30		.40	2.12	8.22	35.42	Pipey through, except lower left.
33	249.9	3.12	145	5.99	20.33	.32	.24	.51	1.91	7.36	33.23	Soft throughout. Spongy at bottom.
34	213.5	2.67	103	6.71	19.34	.30		.51	2.14	8.34	34.29	Firm except bottom.
35	159.8	2.00	74	7.00	17.33	.30		.51	2.22	8.87	35.71	Good throughout, except soft in upper left.
36	182.2	2.28	109	6.32	21.79	.32	.23	.45	2.06	7.17	32.91	Fairly firm on right side. Rest soft.
Average				7.28	17.00	.25		.46	2.35	8.92	34.64	

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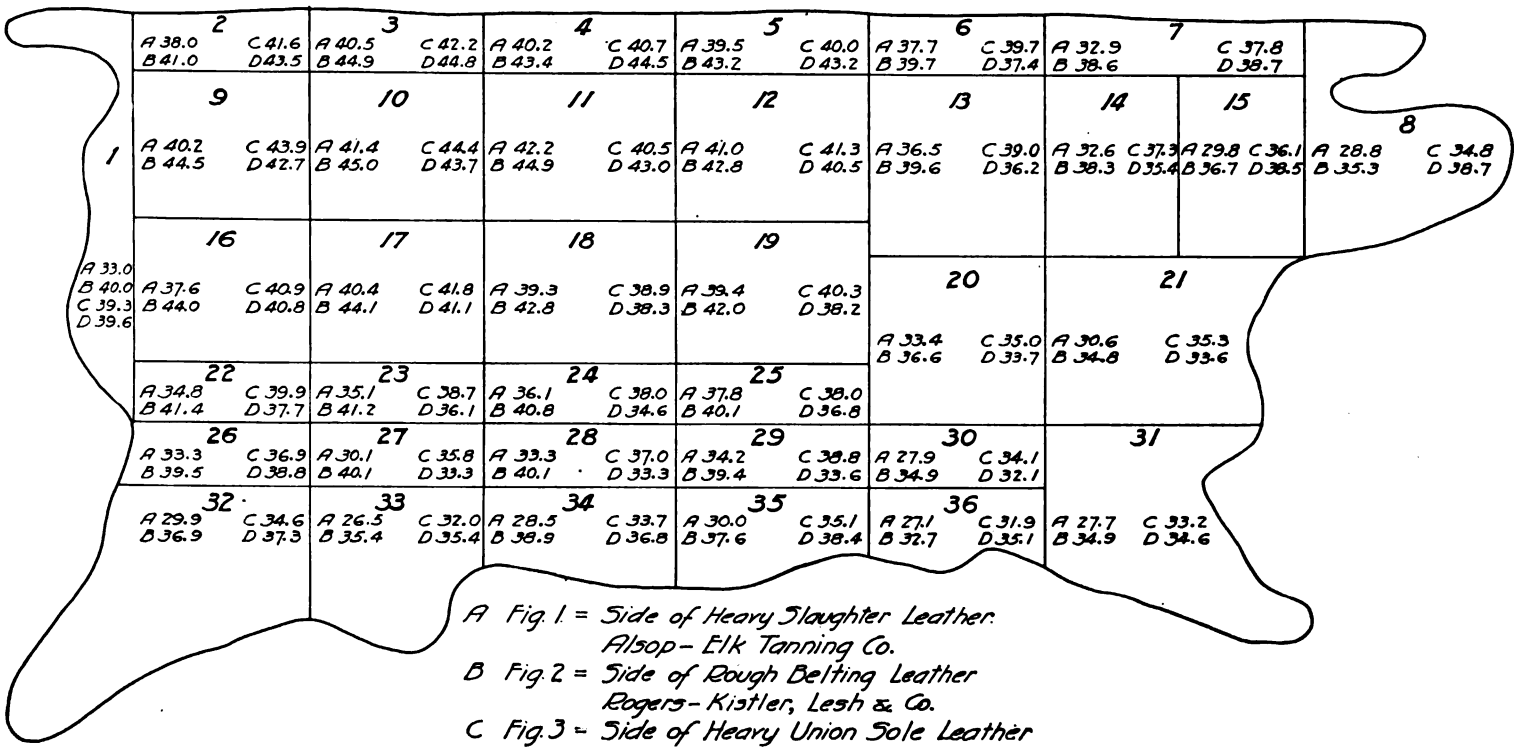
Figure 5

Hide Substance — Moisture Free Basis



A Fig. 1 = Side of Heavy Slaughter Leather.
Alsop – Elk Tanning Co.

B Fig. 2 = Side of Rough Belting Leather
Rogers – Kistler, Lesh & Co.

C Fig. 3 = Side of Heavy Union Sole Leather
Seltzer – Kistler Leather Co.

D Fig. 4 = Side of Curried Belting Leather
Small – Graton & Knight Mfg. Co.

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There is nothing radically new in the results shown in the preceding tables. They bear out the commonly accepted idea that leather varies in composition, that some parts of the hide are looser fibred than others and that they will in consequence carry more load, but it is doubtful whether the universal distribution of the variation or its amount have been fully appreciated.

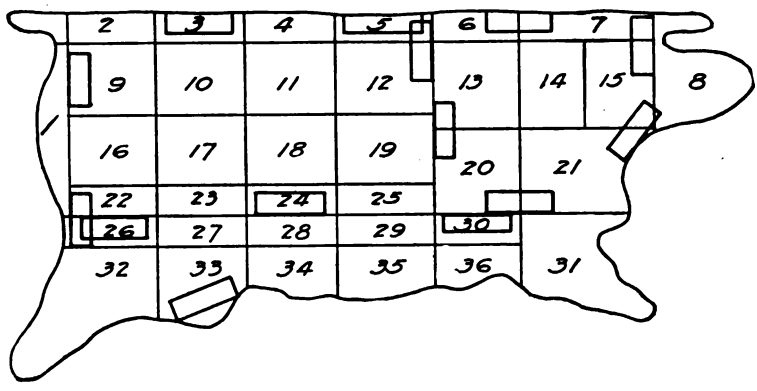
The tabulated figures supply adequate proof that variation in quality, in composition, in analysis, is inevitable in leather and that only as samples are intelligently and carefully taken can they be either comparative or representative. The folly of attempting a comparison of two tannages by analyzing pieces of leather which come from unknown parts of the hide is obvious.

In attempting to deduce from the foregoing data a method of sampling that will give samples accurately representative of the leather sampled, certain fairly obvious principles suggest themselves as demanding observance.

1. The number of samples should be as few as possible.
2. The size of the samples should be as small as possible.
3. The location of the samples should be such as to include parts of the hide divergent in composition.
4. The size and location of the samples should be such as to cause the least damage to the leather by their removal.

Since the method of sampling ought to be applicable to hides of all sizes it is impracticable to specify locations in terms of inches

Diagram showing location of samples suggested.



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from the tail or from the edge, rather must the location be shown in its relation to the dimensions of the hide.

The committee were of the opinion that in general three is the smallest number of samples that can be taken that will include the necessary range of qualities in the leather: that each sample should be 2′ x 8″, the original cuttings being approximately 2½″ x 8″, the ½″ being removed from the uncut edge to avoid irregularities resulting from edge penetration of materials.

On the accompanying diagram is shown the location from which the committee recommends that the various samples should be taken. The particular samples which must be taken to be representative of the various commercial cuttings should be as follows:

	Single	Double
Belly	26-30-33	
Shoulder	(6-7)-(20-21)	(13-20)-(20-21)
Bend	3-5-24	9-(5-12)-24
Butt	3-(6-7)-24	9-(7-15)-24
Side	3-(6-7)-33	9-(15-21)-(22-26)

Illustrating the accuracy that may be possible from the method suggested, there are shown below a few hide-substance figures giving the actual and the calculated percentages as derived from the probable analysis of the samples as shown by the analysis of the cuttings in which the samples are located.

Belly				
Actual	34.2	36.9	36.0	28.9
Calculated	34.7	36.8	35.4	29.4
Shoulder				
Actual	36.6	36.9	36.6	32.8
Calculated	37.0	37.0	36.3	32.4
Butt				
Actual	39.7	41.4	39.5	36.9
Calculated	40.1	41.6	39.5	37.2
Side				
Actual	38.0	39.6	38.5	34.2
Calculated	37.9	40.0	39.5	34.7

It should be stated that the committee believes it much more difficult to sample double or whole bends, butts and hides than single ones. The methods suggested above for sampling these are the best it has been able to devise, but it believes trouble will be experienced in so taking samples that they will be representative and it therefore strongly urges that whenever possible the methods advocated for single butts, bends or sides shall be followed.

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CONDITIONS IN THE LEATHER INDUSTRY.*

By L. J. Robertson

There is very little else to be said after Mr. Small gets through, but the fact that the Council takes official recognition of your meeting today is merely an evidence of courtesy in exchange for the very helpful and constructive cooperation that the Council has received from your Association.

My personal relations with this Association have been more than pleasant and I know that if Mr. Frazier Moffett could have been here to-day he would have been very happy to say a word or two of thanks and appreciation for the very constructive work and assistance which the Committee on Research has received from various prominent members of your Association. I know that the connection made at the University of Cincinnati, notwithstanding a minority report which may be familiar to some of you, was really the result of very careful deliberation and trips made to Cincinnati at naturally some inconvenience. The Council is most grateful for all the help it has received from your Association, and we are especially happy to have Mr. McLaughlin,who really belongs to you by reason of many years of association with you.

After listening to some of the very instructive papers read here, it makes me feel that I have jumped into the wrong pasture lot, and if I can mix my metaphors, I certainly do feel very much like a fish out of water. At the same time, it is perfectly true that unless we fellows can stay in the leather game, we are not going to have very much use for the work that you are doing, and we have got to stick, if for no other purpose than to see that you are occupied.

I took the liberty of preparing a very brief memorandum because prognostications are too dangerous, and with your permission I will just read that to you. Within the past few days, however, one or two matters have occured in Washington which convey a slightly different complexion to one feature that I have referred to very briefly, and that is the matter of tariff. I have a memorandum from the *Journal of Commerce* of a day or two ago, which indicates that a very scant majority — 9 to 8 in other

* Delivered at the 18th Annual Meeting at Atlantic City, June 10, 1921.

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words — in the Ways and Means Committee now prevails favoring free hides. Of course, the shoe man has been right behind the tanner in asking for free hides, but the agricultural interests are pretty strong and they have now come out with a demand that if we are to have free hides. all articles of manufactured leather and leather itself must also be on the free list. It is not for me to criticize the wisdom of that argument, but for the protection of the industry it is the hope of the Council that when the new tariff measure is framed, that we will have protection on leather and free raw material.

When I had the pleasure of meeting Mr. Reed at the Convention of the Tanners' Council about a month ago, I referred to the subject which he had assigned to me and asked him just what he thought I could tell you gentlemen about conditions in the leather trade that you did not already know. Mr. Reed merely answered and said that he felt you wanted to know all about prevailing conditions, and if I may repeat what I then told him, I should like to say that unless things change pretty much, conditions, academically speaking, are about all that we have got in the trade to-day. In other words, to go back to school days when we were burdened with conditions it meant that we had flunked and our industry has certainly flunked badly during the past two years, and is now very busy making up conditions so as to resume its course without any bad marks on its record.

It was particularly gratifying last month here in this same town to find so many tanners and shoe manufacturers sound an optimistic note, and I am sure that the same psychology which caused so many of us to join the majority that could see nothing ahead but wrack and ruin, is causing an even greater number to join those men voicing optimistic views at the present time. In other words, nothing succeeds so well as successs, and if we can secure a return to stabilized prices so that we may safely proceed with the buying of our raw material and the laying out of our industrial policies and in the selling of our merchandise, tanneries will certainly be operating at a profit again instead of at a loss which has been the case for a very protracted period.

Our new administration is apparently doing the right thing to bring this result about. They are giving careful attention to tariff and tax legislation, money rates and to the German situation,

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all of which is bound to increase the confidence of the buying public and thus help our own line get back upon its feet. It is very evident that we are practically within touch of a constructive epoch firmly entrenched upon a much sounder basis than has prevailed for the past eight years, and with a much broader and better spirit of cooperation between the various allied branches of the industry.

Another factor not to be ignored is the attitude of Secretary Hoover, who apparently has determined to make the Department of Commerce something more than merely a name and more what the name implies. Through this department ways and means will be created by which credits can be extended to foreign trade and our export trade correspondingly increased, which in view of the fact that our normal production is excessive for our domestic requirements, is another move towards stabilizing the situation. There is no question about it that one part of the world cannot properly get along without some help from the rest of the world, and while our exports are certainly at a minimum at the present, we have every right and justification in believing that before long we will be getting an increasing demand from overseas for our products.

Of course there are many angles to the situation which can have particular effects upon certain branches of the industry, as for instance, the contemplated duty on raw material, which appears to be fundamentally unsound. Still, we must remenber that various interests are aiming at particular objectives and it appears that the pressure from the agricultural districts is influencing certain of our legislators to do more than merely listen to arguments as to the advisability of levying an import duty on hides. It does not seem wise to follow this policy when we are dependent upon almost 40 per cent of our raw material outside of our own country, as the practical application of this measure would mean in effect that the independent sole leather tanners would have to go out of business and I am hopeful that before the new tariff bill is passed the combined arguments of the shoe and leather allied industries will have met with success and that the Ways and Means Committee will be satisfied and convinced of the injustice accrueing to the industries by the application of such a tariff measure.

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Cooperation between the seller and the customer is also a very helpful factor for bringing conditions back to normal and that feeling of indecision and hopelessness which has existed on the part of the retailer for such a long while is gradually disappearing. While business is still of the hand-to-mouth variety, monthly sales are gradually increasing and we have every reason to believe that we may anticipate a marked increase in production as well as business between now and the end of the year.

It is extremely difficult to operate tanneries the way business is being done to-day. It seems that the shoe manufacturer hesitates to anticipate his requirements for much more than three or four days' mail, and it is very evident that we cannot make up any future stocks in the expectation of new business when the tendency in the retail shops to-day is to change styles as frequently and rapidly as possible in order to stimulate sales. It cannot take very long, however, before we will be back to a condition which will enable the tanners to get into the raw material market with a little more confidence than they have been able to have, and make leather ahead.

In addition to these factors outside of the industry, the tanners are equipping themselves to meet world competition both at home as well as abroad and in such a constructive manner as circumstances indicate may be necessary. I have in mind particularly altruistic efforts for the establishment of research work, tanning school, the elimination of grubs and ticks, cost accounting, the establishment of raw stock bureaus, uniform sales contract and other similar measures which if not absolutely Utopian. mark a very pronounced effort to accomplish the greatest good for the greatest number.

While I am speaking of the greatest good for the greatest number, it seems that your meeting will fail of its full importance unless the tanners generally have an opportunity to benefit by the discussions which have taken place at this meeting and the papers which have been produced. I am hopeful that the Tanners' Council will in a more practical way support the American Leather Chemist Association. And, while the thought only came to me a few moments ago, it seems to me that it is possible of execution and I am quite willing to take the initiative, speaking for the Council, in suggesting that some ways and means should be devis-

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ed by which the annual dues to the Tanners' Council should include a subscription to your Journal. Your Journal is entitled to a much wider publicity among the tanners than it has to-day, and you in turn are entitled to a much greater support from the tanners than you are receiving to-day. Now, if we can have both of these objects taken care of at the same time, I think the Tanners' Council would be benefited annually by giving your Association further evidence of its utility and of the value which the tanners generally throughout the country are willing to concede your services are giving to the industry.

POST-MORTEM CHANGES IN HIDE

By George D. McLaughlin

(FROM THE DEPARTMENT OF LEATHER RESEARCH OF THE TANNERS' COUNCIL, IN THE UNIVERSITY OF CINCINNATI)

The purpose of this article is to show that when a steer dies a rapid change occurs in its hide. The nature of the change, whether chemical or bacterial or both, will be reported later.

Experimental procedure, splitting, weighing, swelling, etc., is the same as that outlined in our last publication.[1] In other words, we have again studied the corium, or true skin. Room temperature averaged 21° C. (70° F.).

We split hide just as it left the steer's body, obtaining sufficient corium for a number of tests. One piece was placed in saturated lime-water (containing excess, undissolved lime as in practical liming) within thirty minutes from the time the hide left the animal. It remained therein one hundred and twenty hours, when it showed a weight gain,which we will call one hundred. Other pieces of the same strip of corium were exposed to room atmosphere for varying lengths of time and then lime. The results are shown in Table I.

TABLE I

Stood	½ hour,	gain	100
Stood	1½ hours,	gain	86
Stood	2½ hours,	gain	76
Stood	3½ hours,	gain	77
Stood	4½ hours,	gain	80

[1] This JOUR., 16, 295 (1921).

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If corium is kept in sealed jars for the periods noted—thus excluding effect of atmosphere and surface evaporation—the results are:

TABLE 2

Stood	½ hour,	gain	100.
Stood	1½ hours,	gain	88
Stood	2½ hours,	gain	88
Stood	3½ hours,	gain	82
Stood	4½ hours,	gain	83

If original hide is allowed to lie exposed to room temperature and is split as needed, the results are:

TABLE 3

Stood	½ hour,	gain	100
Stood	1½ hours,	gain	92
Stood	2½ hours,	gain	78
Stood	3½ hours,	gain	73
Stood	4½ hours,	gain	76

There was no appreciable loss in water by the corium of the unsplit hide used in Table 3, except at its edges, which were trimed off.

An invariable result in all of our experiments herein outlined was the production of a substance which we will call acid by and in the hide. This is easily demonstrated by allowing hide to stand for varying time periods and then splitting and soaking the corium in water. Acid diffuses out into the water. Titrating the soak water with N/20 NaOH, in the presence of phenolphthalein. gives the results detailed in Table 4, which shows the cc. of N/20 NaOH required to neutralize the acid which has diffused out from each one gram of *dry* corium.

The experiments outlined in Table 4 were made at room temperature. If a portion of the same hide as used in Table 4 is kept and soaked at 2° C. (36° F.) we find the results shown in Table 5.

COMMENTS

We note that a rapid change occurs in a hide following the animal's death. This change is manifested by a lowered ability of the corium to swell in lime-water and by the production of acid.

The nature of the acid formed and the mechanism of the change it indicates will be dealt with in the future.

The extent to which these post-mortem changes in hide or skin affect the quality, quantity or cost of leather produced can be

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TABLE 4

	Stood ½ hr.	Stood 1½ hrs.	Stood 2½ hrs.	Stood 3½ hrs.	Stood 4½ hrs.	Stood 24 hrs.	Stood 48 hrs.
After 24 hours water soak	.188 cc.	.280 cc.	.254 cc.	.236 cc.	.282 cc.	.332 cc.	.252 cc.
After 48 hours water soak	.280 cc.	.228 cc.	.198 cc.	.218 cc.	.204 cc.	.246 cc.	.346 cc.
After 72 hours water soak	.424 cc.	.352 cc.	.294 cc.	.344 cc.	.354 cc.	.476 cc.	.932 cc.

TABLE 5

	Stood ½ hr.	Stood 1½ hrs.	Stood 2½ hrs.	Stood 3½ hrs.	Stood 4½ hrs.	Stood 24 hrs.	Stood 48 hrs.
After 24 hours water soak	.078 cc.	.124 cc.	.124 cc.	.112 cc.	.108 cc.	.112 cc.	.122 cc.
After 48 hours water soak	.106 cc.	.114 cc.	.106 cc.	.122 cc.	.106 cc.	.120 cc.	.106 cc.
After 72 hours water soak	.130 cc.	.144 cc.	.140 cc.	.128 cc.	.118 cc.	.122 cc.	.132 cc.

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proved by practical experiment. Such experiments are now under way. One portion of these practical experiments involves giving hide a brine bath of regular salt or a combination of different salts. If post-mortem changes produce undesirable effects we have opened up a fruitful field; if they do not, we have added to scientific knowledge.

THE DETERMINATION OF AVAILABLE CALCIUM OXIDE IN LIME USED FOR UNHAIRING HIDES *

By F. P. Veitch and T. D. Jarrell

LEATHER AND PAPER LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.

The value of lime for unhairing hides depends almost entirely on the available calcium oxide which the lime contains. Relatively few tanners, however, pay attention to the quality of the lime they use with the result that much low grade lime is used in tanneries and the total cost of lime for unhairing may be at times twice as great as it should be. Tanners should buy lime on specifications, requiring a minimum percentage of available CaO, and should test each delivery to see that it complies with the specifications. A high grade lime is, of course, generally to be preferred. However, limes containing as little as 50 per cent of available lime can be used but should not cost the tanner as much as limes containing more available CaO.

A number of methods have been proposed for determining the available lime in burned lime and hydrated lime. Probably the oldest of these and certainly the one in most general use in tanning laboratories is that described by Procter ("Textbook of Tanning" (1885), p. 102), ("Principles of Leather Maufacture" (1903), p. 125). This method is based on the solubility of calcium oxide in water and the titration of the clear calcium hydroxide solution with standard acid. Procter does not describe this method in sufficient detail for an analyst to follow it intelligently, nor to enable him to secure constant, concordant results.

Stone and Schench (*Jour. Am. Chem. Soc.*, **16** (1894), p. 721), Hendrick (*Analyst*, 13 (1907), p 320), Croghan (*Jour. Chem. Met. and Min. Soc. of S. A.*, 8 (1907), p. 37), and Meikle-

* Read at the 18th Annual Meeting at Atlantic City, June 11, 1921.

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john (*Jour. Chem. Met. and Min. Soc. of S. A.*, **19** (1918), p. 85), and (*Eng. and Min. Jour.*, **107** (1919), p. 739), and others have published results based on solubility of calium oxide in a sucrose solution and titration with standard acid.

Lunge ("Techno-Chemical Analysis," Cohn (1905), p. 67), ("Technical Methods of Chemical Analysis," Keane, Vol. I, part I, (1908) Ed., p. 483)describes a method for estimating the active calium oxide in lime by adding to the milk of lime solution phenolphthalein and then titrating it with normal hydrochloric acid until the color disappears. The same method is described in Lunge's "Technical Chemist's Handbook (1908) Ed.), p. 156, and (1916 Edition), p. 158, except that the milk of lime solution is titrated with oxalic acid instead of hydrochloric acid.

Bahney (*Jour. Ind. and Eng. Chem.*, **2** (1910), p. 407) titrates a milk of lime solution with standard oxalic acid, practically as directed by Lunge (loc. cit.) but describes the procedure in more detail. This procedure was tried by the authors but discordant and unreliable results were obtained, especially on limes containing considerable magnesia. Croghan (loc. cit.) has already pointed out the difficulty of obtaining reliable results by the direct titration of free calium oxide in a milk of lime solution when much magnesium oxide is present.

Little and Beisler (*Jour. A. L. C. A.*, **14** (1919), p. 613) propose to ignore small quantities of sodium or potassium hydroxide which may be present in the lime. The clear lime water solution is precipitated in the usual manner as calcium oxalate, the precipitate dissolved in sulphuric acid and the solution titrated with standard potassium permanganate. The possible presence of calcium chloride or calcium sulphate in some limes is apparently ignored. Results by their proposed procedure would be higher than the usual titration method if these salts are present and sodium or potassium hydroxide is absent. It is also too long and involved for a control method.

Since the value of lime for unhairing hides is based on its alkalinity derived primarily from the available CaO or more soluble alkalies present, it is believed that the small quantities of sodium or potassium hydroxide which may be found in some limes is not objectionable.

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In caustic soda works a method based on conversion of calcium hydroxide to sodium hydroxide by the addition of sodium carbonate free of bi-carbonate to the milk of lime solution is sometimes used, The excess of sodium carbonate is precipitated as barium carbonate and the sodium hydroxide titrated with standard acid, using phenolphthalein as indicator. This method was tried here on several samples but all results were low, due probably to the formation of a coating of calcium carbonate over the undissolved calcium hydroxide, under the conditions of the procedure employed, which prevents the completion of the reaction between the undissolved calcium oxide or hydroxide. Assuming that this method will give accurate results, it is more involved and has no apparent advantage over the methods described subsequently in this paper.

The method generally used in tannery laboratories is that described by Procter (Leather Industries Laboratory Book, p. 54) chiefly, doubtless, because of its simplicity and similarity to actual working conditions. This method as given in various text books, is not stated in sufficient detail to insure obtaining accurate results with it. In a study of methods for determining available CaO in limes it was soon found that fineness of division and agitation are the essential, controlling factors in this method. These should be specifically stated if agreeing results by different analysts are to be obtained.

These factors have been carefully worked out and some of the data are presented in this paper. The Schaife method, which is used somewhat extensively, has also been studied. Here too, fineness of division has much to do with concordant, accurate results.

These methods were selected for study because they are simple to manipulate and because experience indicated that the results obtained with them would show quite accurately the true alkalinity or available CaO of the lime at the time of analysis.

After considerable experimental work the following detailed procedures were finally adopted.

Method I. Modified Tannery Method. Place 1 gram of the thoroughly mixed sample, ground to pass a 60 mesh sieve, in a graduated liter flask; add about 10 cc. of hot freshly boiled dis-

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tilled water and shake well. After the lime has slaked, add about a dozen small glass beads and about 950 cc. of freshly boiled distilled water of room temperature, stopper and shake. 6 times for 5 minutes each at intervals of 1 hour. Fill to the mark, mix thoroughly and allow to stand until practically clear or over night. Carefully pipette 100 cc. of the clear solution into an Erlenmeyer flask; add several drops of phenolphthalein solution and titrate at once with N/10 hydrochloric acid, and calculate to available CaO.

Method II. Modified Scaife Method. (1) Place 1.4 grams of the thoroughly mixed sample ground to pass a 100 mesh sieve into a 250 cc. beaker, add about 150 cc. hot water, cover, heat carefully and then boil for 3 minutes.

(2) Cool, wash down cover, add two drops of phenolphthalein and titrate with normal hydrochloric acid, adding the acid as rapidly as possible by dropping, stirring vigorously to avoid local excess of acid. When white spots appear, add the acid somewhat more slowly, but continue until the pink color *fades* out *throughout* the solution for a second or two. Note the amount of acid used and ignore the return of color.

(3) Repeat the experiment using a 500 cc. graduated flask instead of a beaker, add 4.5 cc. less normal acid than before, designate the number of cc. used as "A." Grind up any small lumps with a glass rod slightly flattened at one end, dilute to the mark with distilled water, mix thoroughly for five minutes, and let settle for one-half hour.

(4) Draw off 100 cc. of the solution without filtering, add phenolphthalein and titrate with N/2 hydrochloric acid, designate this additional number of cc. as "B." Per cent of available CaO= 2A + 5B.

The effect of the fineness of the sample and of agitation on the determination are strikingly shown in Table I. For this work a sample was chosen on which it was particularly difficult to obtain consistent and concordant results. It was a quick lime containing 73.4 per cent CaO, 5.5 per cent MgO, and 11.8 per cent insoluble matter. This sample as received in the laboratory had been ground to pass a 20-mesh sieve; 55 per cent passed a 40-mesh sieve

The results show the difficulty of obtaining concordant results on this sample unless it is ground sufficiently fine and the solution

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TABLE I. EFFECT OF FINENESS AND AGITATION ON DETERMINATION OF AVAILABLE LIME BY METHOD I.

Sample No. 1. Method of Shaking	20 Mesh	40 Mesh	60 Mesh	80 Mesh	100 Mesh
		Per cent available CaO.			
Shaken 5 min.	39.3	41.8	51.9	54.4	57.2
Shaken 10 min.	46.0	46.3		58.1	60.0
Shaken 5 min. stood 3 hrs., shaken 5 min.		51.9	57.5	60.9	63.7
Shaken 10 min. stood 3 hrs., shaken 10 min.		57.8	64.5	64.8	65.1
Shaken 5 min. stood 3 hrs., shaken 5 min. stood over night Shaken 5 min.		60.0	65.1	65.2	65.3
Shaken 5 min. stood 3 hrs., shaken 5 min. stood over night. Shaken 5 min.		60.6	65.1	65.1	65.3
Stood 3 hrs., shaken 5 min.		64.5	65.2	65.1	65.3
Shaken 10 min. stood 3 hrs., shaken 10 min. stood over night. Shaken 10 min., stood 3 hrs., shaken 10 min.			62.8		
Shaken 6 - 2 min. periods, at 1 hr. intervals			65.3		
Shaken 6 - 5 min. periods, at 1 hr intervals					
Shaken 6 - 2 min. periods, at 1 hr intervals			64.5		
Stood over night, shaken 2 min. at 1 hr. intervals.			65.3		
Shaken 6 - 5 min. stood over night, shaken 5 min.					
Shake in rotary shaker for five hours (10 revolutions per min.)			65.3		

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shaken for a long time. The figures indicate that excellent results are obtained when the sample is ground to pass a 60-mesh sieve and the solution shaken for six 5-minutes periods, at intervals of one hour, or when it is shaken for 5 hours continuously in a rotary shaker making 10 revolutions per minute. It should not be understood that this long shaking is required for all samples of lime; in fact most of the samples tested required but 10 minutes vigorous shaking in order to obtain maximum results for available CaO. To insure the maximum results on any sample of lime passing a 60-mesh sieve, it is advisable to follow closely the directions for shaking.

In Table II are given results by Methods I and II on various

TABLE II. COMPARISON OF THE MODIFIED TANNERY AND THE MODIFIED SCAIFE METHODS.

Sample No.	Composition of lime			Method I. Modified tannery method	Method II. Modified scaife method
			Per cent.	Per cent. available CaO	
2 Quick lime	Total	CaO,	91.6	84.6	84.6
		MgO,	1.9		
	Insoluble		1.2		
3 Hydrated lime	Total	CaO,	69.5	58.9	59.3
		MgO,	2.0		
	Insoluble		1.0		
4 Hydrated lime	Total	CaO,	45.5	37.3	37.5
		MgO,	32.0		
	Insoluble		0.2		
5 Quick lime	Total	CaO,	57.9	55.8	55.8
		MgO,	40.5		
	Insoluble		0.7		
6 Quick lime	Total	CaO,	93.0	80.5	80.0
		MgO,	1.5		
	Insoluble		0.5		
7 Hydrated lime	Total	CaO,	72.8	60.3	60.4
		MgO,	3.4		
	Insoluble		2.5		
8 Quick lime	Total	CaO,	75.6	61.1	60.9
		MgO,	3.1		
	Insoluble		5.9		
9 Quick lime	Total	CaO,	48.3	40.1	40.0
		MgO,	34.9		
	Insoluble		3.2		
10 Quick lime	Total	CaO,	79.5	59.4	59.7
		MgO,	40.4		
	Insoluble		11.9		
11 Quick lime	Total	CaO,	86.7	81.3	80.8
		MgO,			
	Insoluble		7.4		

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samples of lime. All the samples were ground to pass a 60-mesh sieve.

All the figures recorded in this table under Method I represent maximum and concordant results obtained by continous shaking for 5 hours. Several of the samples gave maximum results by this method when shaken for 5 minutes, allowed to stand 3 hours and again shaken for 5 minutes. Other samples required longer shaking. All samples tested gave maximum results either when shaken by hand for six 5-minute periods, at intervals of one hour or when shaken in a rotary shaker continuously for 5 hours.

The results by Method II compare very favorably with those by Method I. Method II require more skill and practice to manipulate it because the preliminary titration is made in milk of lime solution and it is difficult to determine the end-point especially when considerable magnesium oxide or carbonate is present in the lime.

It is believed that Method I is somewhat less liable to error than Method II, but that results can be obtained in a shorter time by the latter. It should be remembered, however, that the lime must be ground to pass at least a 60-mesh sieve and the solution must be shaken sufficiently long to insure all the CaO present going into the solution. As already pointed out, while this time may vary considerably, depending on the physical condition of the sample, five hours continuous shaking or shaking six times for 5 miutes each at intervals of 1 hour, has been found to be sufficient for all samples of lime so far examined.

ABSTRACTS.

Depsides and Tannins. By K. FREUDENBERG, *Coll.*, 10-19, 1921, *J. S. C. I.* **40**, 312 A (1921). A HISTORICAL account of Fischer's synthesis of gallotannic acid and tannin-like substances. Carbomethoxybenzoic acid was prepared from *p*-hydroxybenzoic acid and was converted, by means of the Schotten-Baumann reaction, into an ester anhydride of *p*-hydroxybenzoic acid. This was termed a depside. By partial saponification of triacetylgallic acid to diacetylgallic acid and combination of the free hydroxl group with triacetylgalloyl chloride, a penta-acetyl-*m*-digallic acid was obtained, which proved to be a true tannin, like the corresponding didepsides of the dihydroxybenzoic acids. There yet remained the 7 per cent of dextrose obtained from gallotannlc acid, which was not easily liberated, and hence

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was not present in the form of a glucoside. The absence of free carboxyl groups in gallotannic acid indicated that the carboxyl groups in gallic acid were united to the hydroxyl groups in the dextrose. Fischer and Bergmann prepared pentadigalloylglucose and found it very similar to Chinese gallotannic acid. It was not identical, since the natural product consists of a mixture of isomers, whilst the synthetic product was a single subtance. The synthesis of fully methylated gallotannic acid was also effected. The comparison of pentagalloyglucose with Turkish gallotannic acid was rendered difficult owing to the presence of an ellagic acid tannin in the natural product. Glucogallin, a constituent of rhubarb, was identified by Fischer and Bergmann as 1-galloyl-ß-glucose, and was synthesised from acetobromoglucose and silver triacetylgallate. Fischer worked out a new method for preparing partially acetylated glucose derivatives. Two molecules of acetone are combined with one of dextrose in presence of a little hydrochloric acid, forming a diacetoneglucose. The free hydroxyl group is combined with an acid chloride and the acetone is split off one molecule at a time. Futher developments have been along the lines of analysis with tannase which has helped to explain the constitution of chlorogenic acid ($C_{16}H_{18}O_9$). By its aid, hamameli-tannin was shown to consist of a new sugar esterified with two molecules of gallic acid. Chebulinic acid from myrobalans contains a digalloylglucose combined with an unknown acid. There are four groups of tannins, ester tannins, catechins, oak and chestnut, and ellagic acid tannin. Crystalline tannins are difficultly soluble in water, amorphous tannins are more readily soluble.

Resistance of Anthrax Spores to Chlorine, Pickling Liquors, Formaldehyde and Mercuric Chloride. By A. MULLER. *Arch. Hyg.*. 1920, **89**, 363—372. *Chem. Zentr.*, 1921, **92**, I, 501. *J. S. C. I.* **40**, 319 A (1921). A 1.5 per cent CHLORINE solution killed the spores in 8 hours, 0.5 per cent solution in 21 hours. A pickle containing 0.5 per cent of hydrochloric acid was ineffective even after 31 days, 4 per cent hydrochloric acid solution at 37° C. killed the spores after 2 days, 2 per cent hydrochloric acid after 6 days, 1 per cent and 0.5 per cent after 7 days, 0.5 per cent formaldehyde solution killed the spores in 6 days, 5 per cent in 5 days; 0.1 per cent mercuric chloride solution was ineffective in 1 day, and 2 per cent solution in 88 days. At 37° C. 0.1—5 per cent solution of mercuric chloride killed the spores in 20—5 days.

Evolution of Different Methods of Tanning. By URBAIN J. THUAU, *Le Cuir*, 10, 80 and 102 (1921). In a brief review of the evolution of different methods of tanning presented at the Feb. 7, 1921, meeting of the French Section of the Society of Leather Chemists, the author makes an appeal for more practical discussions and papers in order to attract the interest of the tanners. Tanning, unlike many industries, has undergone numerous fundamental changes particularly in the introduction of new tanning materials. Chief among these are undoubtedly the salts of chromium and it remains

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to be seen whether this represents the end of an evolution or simply a transition leading to new methods of tanning as superior to chrome as the latter is to the ancient methods. Alum tannage, the oldest of all mineral processes, and at one time in great favor for glove tannage is being replaced by more modern processes such as chrome and formaldehyde. In chrome tannage the one bath process is now generally used although the two bath method is still exclusively employed for kid and for certain heavy leathers, such as whips and for pneumatic leathers, principally because of the extreme suppleness imparted by the free sulphur deposited between the fibers. This property of sulphur is utilized in the sulphur "tannage" which consists simply of treating the skin after pickling in a concentrated bath of sodium thiosulphate. Since the skin is dehydrated by the strong thiosulphate solution it can be readily greased or stuffed. It would be interesting to determine whether or not the oils actually combine with sulphur "tanned" leather. True tannage with sulphur does not occur and in practice such leathers are generally given either a light vegetable or chrome retannage. Sulphur tanned leathers possess a high degree of resistance and are extremely pliable. One bath chrome liquors are made with chrome alum, chromium chloride or organic salts of chromium such as the formate or butyrate rendered sufficiently basic by the addition of sodium carbonate or by simply dissolving chromium hydroxide in the appropriate quantity of acid. Chrome liquors are also made by reduction of chromic acid either by organic substances such as glycerine, glucose, sugar, dextrine or cellulose materials or by inorganic compounds as sodium thiosulphate, sulphite, bisulphite or sulphurous acid.. Before the war the formate, butyrate and even the basic acetate of chromium were used to some extent but the price of these is now prohibitive. The cutting off of chrome alum from Germany during the war led to a pretty general development of one bath chrome liquors with sodium dichromate as a base.. Such liquors formed by reduction with organic materials are to be preferred over those from reduction by sulphurous acid. Products of an aldehyde nature from the decomposition of the organic matter have some tanning value and the incompletely transformed organic matter also plays an important role in imparting to the leather a certain degree of softness and pliability. The presence of neutral salts has an important bearing on the amount of swelling and the rate of tannage. The chromium compound in the tanned leather is more basic than the liquor in which it was tanned, which is also shown by the used liquors becoming less basic and requiring adjustment of the basicity. In Central Europe during the war iron tannage was used with satisfactory results. The principal criticism of iron tannage is that it produces a brittle grain due to difficulties of neutralization. Detannization occurs during neutralization and insufficient neutralization leaves uncombined acid salts of iron in the leather making it brittle. Processes exist, however, for correcting this fault. Despite the low cost of iron tannage. it is not believed that it will replace chrome tannage. For certain purposes, however. a combination of the two may prove valuable. In iron

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tannage the skins are pickled and tanned similarly to chrome in one bath with basic iron solutions. This liquor is prepared by oxidizing 12 parts of slightly acidified 33 per cent ferrous sulphate with 3 parts of a 10 per cent sodium chlorate solution, keeping the temperature below 35° C. There is obtained an iron solution containing 8 to 10 per cent ferric oxide and an excess of at least 10 per cent of the quantity of oxidizing agent used. After tannage complete neutralization is effected with an alkaline material insoluble in water. Analogous to chrome are the elements molybdenum, tungsten and uranium but it is not probable that sufficient quantities of these ever will be available to make their use practical. Silica tannage, discovered by Hough, offers possibilities especially as silicon is one of the most abundant elements. The tannage is carried out with silicate of soda or potash and a mineral acid in the following proportions for 100 kg. of white weight; 50 kg. sodium silicate of 36 Bé and 17 kg. hydrochloric acid. With these quantities 25 kg. of sea salt can be added and the solution diluted to 500 liters with water. During tannage it will be necessary to frequently add the silicate and acid. The resulting leather is perfectly white and must be neutralized and oiled as for chrome leather. It is interesting to note that a great deal more silica is taken up and combined with the leather than is the case with chromium oxide in the chrome tannage. One serious fault of the silicate process is that the leather after some months and often before that, tears very readily, due no doubt to the action of the silicic acid on the fiber. Some day this fault may be corrected and then it will not be out of place to suppose that silica tannage will replace the chrome processes especially because of its cheapness. At present there is no probability of this, although even now a combination of silica and chrome tannage possibly could be advantageously used. The salts of manganese and even of zinc have been spoken of for tanning, but experiments so far have not given encouraging results.

The evolution of vegetable tannage from the old time layaways to the rapid tannage with extracts was accompanied by many failures through lack of experience. Not only were many of the extracts poorly decolorized but it was not realized that it was necessary to thoroughly delime and that the leather from the drums had to be freed of excess of extract before drying or it would become brittle and dark. These difficulties have been overcome and now a good leather can be made by rapid tannage. Such leather, however, does not give sufficient yield and experience has shown that this can be increased by drying the leather and retanning with special highly decolorized extracts which makes washing of the leather from the drum unnecessary. While this may give a good yield and often a certain quality of fullness and firmness it has been criticised on the ground that such leather contains an excessive amount of tannin not combined with the hide. Up to the present high combined tannin has only been obtained by layaways of 2 to 3 months. Leaving a rapidly tanned leather for 3 months in a vat of oak bark and tan liquor is not the same thing as leaving the leather for the same period in a tan liquor alone of the same strength as that

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in the bark vat. The combined tannin will be higher in the case of the bark and liquor so that the bark plays a role which is not known. Whether it is one of an electrical, physical, or bacterial nature or plays a part similar to that of a catalyser in favoring for example the oxidation of the hide fiber remains to be shown. It is hoped that this question will soon be answered for then it may be posslble to successfully replace the old vat tannage with a more rapid and scientific method.

Among the innovations of a physical nature in vegetable tannage are agitation of the liquors, increase of temperature of the liquors and utilization of vacuum and of pressure. Agitation with the liquors between 30° to 36° C. has proved satisfactory for some. At this temperature the insolubles in the liquors are greatly reduced. Tanning with vacuum has been proposed often but was not satisfactory until the invention of an efficient pump by Nance. Removing all the water and air from the hide before tanning gives a perfect dehydration so that a very rapid tannage even with weak liquors takes place. This gives however a low yield and led to the replacing of vacuum tannage by tanning under pressure in autoclaves with liquors freed of air. By this means as much tannin as is desired can be made to penetrate the leather. Before tanning under pressure the hides are freed of water and air by vacuum. The slight solubility of some tannins has been utilized by certain tanners in finishing the tannage or even in retanning with warm solutions which are difficultly soluble upon cooling thereby giving to the leather a greater resistance to water at the ordinary temperature.

Among the recent advances of a chemical nature are the use of formaldehyde in fixing the grain to avoid wrinkling in drum tanning; of quinone as a preparatory tannage; of pyrophosphate of alumina as a pretannage; of viscous colloids like gum tragasol and starch paste as vehicles for the tanning extracts; and of other chemicals, particularly the synthetic organic tannins, as pre-tannages or assistants.

The synthetic organic tannins should be distinguished from the synthetic vegetable tannins such as those of Emil Fischer. The oldest synthetic organic tannage is undoubtedly that of formaldehyde. This process has not met with as much success as was hoped for, the main criticisms being that the leather does not resist the action of boiling water and upon ageing some tears readily. It is utilized in making washable white chamois for gloves, the quantity of formaldehyde varying from 1 per cent to 1.5 per cent of the white weight,while the proportations of soda and thiosulphate are varied according to the tannage. Substitution of acetaldehyde and even of paraldehyde for formaldehyde has proved satisfactory. In 1908 Meunier and Seyewetz published their discovery of the precipitation of gelatine by quinone. Quinone tannage has not received the development that it deserves and some day its use on a large scale may not be surprising. For tanning by oxidation the use of bromine, chlorine, iodine, hypochlorites, Javelle water, hypobromites, and chloride of lime has been suggested

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but practical results have not been obtained. Stiasny's discovery of "syntans" by condensation of sulphonated phenols led to the manufacture of many other similar products either from phenol, cresol, naphthalene or anthracene. In England these products are called "Synan D. and D. M.," "Maryntan," "Paradol," and so on, in America the most favored one is "Talide." Very satisfactory products also have been made in France but it is in Germany that their manufacture has been most extensive and to-day the Badische Anilin and Soda Fabrik, having purchased the patents of Stiasny, are manufacturing numerous materials of a varied nature, including "Neradol D," a condensation product of cresol sulphonic acid, "Neradol N" a condensation product of naphthalene sulphonic acid and "Ordoval G." Grasser has shown that the bakelite products dissolved in alkali and alcohol precipitate gelatine and tan hide especially after neutralization. It is believed that the synthetic organic tannins will be of importance in future tanning. By mixing them with tanning extracts to the extent of 5 per cent to 10 per cent of the extract they dissolve most of the insolubles, and improve the color. They can be used in the solubilisation of quebracho and as a pre-tannage. Mixed with the tan liquors they give good color and plumpness.

R. W. F.

Patent Leather. Anonymous, *Ledertech. Rund.* **12**, 113 and 121 (1921). In general the tannage of patent leather is secondary to the quality and fineness of the enamel, but the purpose for which the leather is to be used determines the importance of the tannage. Shoe leather should have a soft feel and is therefore retanned with a modified dongola-fat after tannage, because a complete vegetable tannage only contains a little grease. For 10 cowhides, 1 pound of alum and ½ pound of salt is added to warm sumac liquor and the leather drummed in it about 20 minutes. It is an advantage to strip the leather previously with luke warm water and borax for ½ hour and then wash in pure water. After the above retannage the leather is given 5 pounds of soap and ½ liter of light train oil in water at 35° C. either in the rotating drum for several hours or in the handlers for 12 hours. The leather is then spread out and lightly oiled with light train oil. After drying it is moistened again and carefully shaved, then thoroughly moistened again (best with sumac liquor), reset on the table and oiled lightly on the grain with dégras. After drying, the grain is buffed and the leather is ready for enamelling. Calf leather is enamelled on the flesh side and therefore this must be whitened. For enamelling, the leather is first stretched on frames whose size should correspond to the work tables, rooms and doors. The room must be completely free from dust. The enamelling is divided into three operations, grounding black varnishing and enamelling proper. The grounding which is carried out by means of a round, short haired brush, gives the ground by rubbing it well into the surface of the leather. Only as much is applied as the grain is able to absorb. After the ground is applied the leather is dried in the sun where it must be protected from dust and rain. As soon

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as the coating is dried well (usually on the following day) the whole surface is rubbed with fine, artificial pumice in order to remove contingent unevenness and to make the surface completely smooth. Before rubbing, the ground must be completely dry as it easily comes off. Then the dust is washed off with luke warm water and chamois leather and dried well again. Then the grounding, drying, rubbing, washing off and drying is repeated with a somewhat lighter coating than the first time. Enamelled leather is then black varnished while japanned leather is still oftener subjected to the procedure of grounding, rubbing, etc. In black varnishing, the frames are placed horizontally on two horses, the leather is brushed off again, and the blacking applied with a broad brush. The oven is heated to 40° C. and the black-varnished leather, grain side up, is placed in. When the oven is full the temperature is raised to 50° C. and held for 12 hours. After this time of drying it is very important to place the frames in the sun until the varnished side is no longer sticky. The leather is then taken from the frames and rubbed smooth on a table covered with felt by means of artificial pumice No. 2, both sides brushed out well and again placed in the frames, washed off with chamois and luke warm water, dried well, dusted off and enamelled. This coating is applied with the most careful precautions in a completely draft-and-dust-free room by means of a fine horse hair brush. Lately the spray is being employed more and more for this purpose.

The requirements which are placed on a good, serviceable leather enamel are of various kinds. It must intimately unite with the leather fiber so that cracking and peeling is excluded; it shall dry well, so that at high temperatures it is not sticky, it shall be flexible and neither by cold or long wear show breaks or cracks but must correspond to the elasticity and tension of the leather. Further, the enamel must be water-proof and possess a high luster. In order to bestow the above properties on the enamel, the linseed oil and chemicals must be of the choicest quality. Linseed oil to be used for the preparation of the enamels should be stored for at least 3 months. The characteristics of such are yellow color and transparency while oil stored for a short time has a green and turbid appearance.

The ground for the first and second coat is produced as follows:— 100 pounds of old linseed oil is cooked 24 hours until it has reached the temperature of 200° C. During this time 100 grams of litharge (Goldglätte) is stirred in. After the time given 150 grams of paris blue, 650 grs. manganese borate, 250 grs. manganese carbonate and 50 grs. talcum are stirred in. During this addition it must be unceasingly stirred to prevent boiling over. When it is all well mixed, the heat is raised to 250° C. meanwhile stirring frequently to prevent formation of sediment on the bottom. Several drops are tested on cold glass. If they are so thick when cooled that they can be drawn out then the mass is ladled and stirred until it is as thick as dough. The fire is then removed, the kettle carried into the air and stirred again for a

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quarter of an hour. When it has cooled somewhat, 50-60 kg. turpentine warmed on the water bath to 50-60° C. are slowly added to, and intimately mixed with it. After cooling, the whole is emptied into a sheet iron cask with a tight lid to exclude air and other exterior influences. For use, 6 pounds of this ground is well kneaded with 200 grs. lampblack and enough turpentine so that the paste can be spread well with the brush after passing it several times through the triple-roll mill.

For black varnish 100 kg. of linseed oil is heated with 300 grs. litharge at 220° C. for 1-2 days and then is added in turn: sugar of lead 2 kg., manganese borate 1 kg., manganese oleate 0.5 kg., lampblack 4 kg. After the last addition the temperature is raised to 250-260° C. and held at this temperature until, while hot, it has the consistency of coal tar and when cold, a drop on glass can be drawn out in a thread 5 to 6 cm. long. When this point is attained, the contents are run out and cooled without the addition of turpentine. For diluting the black varnish, 50 kgs. are diluted with 80 kgs. of turpentine, then 2.5 kgs. of lampblack are added and the whole passed through the dye mill 3 or 4 times. Before use it is filtered through fine gauze covered with wadding, diluted with the necessary amount of turpentine and stirred several minutes.

The production of the enamel follows in a similar manner. After 100 pounds of old linseed oil is boiled down at 200° C. for two days in the usual manner with 100 grs. of litharge, there is stirred in with constant motion 3 pounds of paris blue, 1 pound syrian asphalt, 1 pound manganese carbonate and 50 grams of verdigris whereby care must be taken to prevent boiling over and formation of sediment on the bottom. Then the temperature is raised to 280° C. and the enamel allowed to rise once or twice to a temperature of 300°. When the temperature has been raised several times then the cooking is continued at 280° until several test drops, cooled on glass, can be drawn out in threads. When the enamel is good it is taken from the fire and cooled down to 80°-100° C. 100 pounds of turpentine are added to it and stirred vigorously until the whole is well mixed. The whole is then placed to settle in the warm oven. It is diluted further for use.

Japan ground is produced when 100 pounds of old linseed oil is boiled down for two days at the usual temperature with 100 grs. of litharge and then 2 pounds of manganese carbonate, 1 pound of white lead and 5 pounds of dark umber cooked in. For use, into 20 pounds of the stock ground is mixed 4 pounds of the finest yellow ochre and 1½ pounds of lampblack while only sufficient turpentine is added to it so that when it is ready for use it is still thick. The preparation of japan is the same as for enamel only it is prepared somewhat stronger by the addition of less turpentine. For acidifying japan lacquer, sulfuric acid is frequently used as follows: 1 liter of turpentine is poured into a long handled, large porcelain ladle and about 40-50 grs. of pure sulfuric acid is slowly added and stirred with a glass rod until the turpentine boils,

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then the acidified oil is immediately poured into the lacquer, stirred thoroughly and filtered through fine mesh gauze into another container. After the japan is filtered it is again placed in the oven taking care to avoid any kind of a jar or blow. After 2 or 3 weeks it is ready for use. By being stored for some months the lacquer gains materially in lustre. elasticity and durability. Through dilution with turpentine it can be regulated according to desire. The thinner, so much the less glossy will it be. Japanned cowhides are once or twice grounded, once black varnished, and 2 or 3 times enamelled;japanned splits are grounded, black varnished and enamelled oftener.

Enamelled leather is put into the oven at 25° C. When the oven is full, the temperature is raised to 55° C. and the leather should be dry in 15 to 18 hours. Then it is placed in the air or sun for ½ to 1 day in summer but for a shorter time in winter. Boarding is carried out on a fine graining board with cork cushion. It is recommended not to press too hard since a lighter pressure gives the best results. After boarding the leather should again be placed in the frames in a warm room for about a week. It is then taken from the frames, dusted off, trimmed, hung up and for storing is horsed up with the grain side in.

Washable japanned upholstery leather should be as soft as fabric and therefore attention is given to the tanning and finishing to accomplish this end. Vegetable tanned leather is partially stripped by drumming in a lukewarm solution of borax or soap and then washed in pure water. It is then given either a dongola-fat or a chrome retannage. Proper oiling plays a very important part in producing a soft leather. For this purpose train oil and dégras are the best. The greatest part of the fat is removed from the leather later by means of benzine, carbon tetrachloride or trichlorethylene. The whitened leather stretched on frames is first given the ground, dried well and then smoothed off with natural pumice, dusted off with chamois leather and polished. The application of the second ground follows which is also dried well (as much as possible in the sun) followed again by careful rubbing, dusting and polishing. The color coat is next applied with a broad brush, first toward the sides, then from head to tail and finally transversely in order to prevent streaks. The leather is then placed in the oven at a temperature of 35° C. The temperature is raised to 55° C. and held at this until the leather is completely dry. When the color coat is dry, the leather is allowed to cool and then it is rubbed with fine natural pumice, the dust completely removed and another coat of color given in the same manner. After drying this time the color layer is not rubbed but the leather is thoroughly brushed off and with quick, uniform strokes it is given either the furniture or automobile enamel according to whether a dull or high lustre is desired. The enamelled leather is placed in the oven at a temperature of 55° C. which is increased several degrees at the end. After the leather is completely dry it is allowed to age 5 days whereby the layer of enamel gains in flexibility and elasticity. Then the desired grain design is printed and then lightly boarded.

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To make the first ground—100 kgs. of old linseed oil is heated for a day at 200° C. with 250 grs. litharge (Goldglätte) and then is added in the following order 1.0 kg. sugar of lead, 1.0 kg. manganese borate, 0.4 kg. manganese oleate and 1.0 kg. cobalt resinate. After the addition of the last named the temperature is gradually raised to 270° C. and held until a drop on glass draws out in a long thread. When this point is reached the contents of the kettle is ladled until it becomes so thick it appears porous and does not adhere to the sides of the kettle. Then it is taken from the fire and worked further until the temperature has fallen to 150° C. 100 kgs. of turpentine are added with constant stirring until an intimate mixture is obtained. For use about 3 parts of this is mixed with 1 part turpentine, however, if this is still too thick to apply after passing through the mill several times, it is thinned with sufficient turpentine.

To make the second ground—100 kgs. of old linseed oil is cooked for 1 day at 200° C. with 300 grs. of litharge and then 1.0 kg. sugar of lead, 1.0 kg. manganese borate, 0.4 kg. manganese oleate and 1.0 kg. cobalt oleate are stirred in. This ground is not cooked so thick as the previous. It should be softer and more transparent.

To make the varnish for the color coating—100 kgs. of old, bleached linseed oil is heated for 1-2 hours at 200° C. with 500 grs. litharge and 0.5 kg. sugar of lead, 0.5 kg. manganese borate and 0.5 kg. cobalt oleate are successively added. After the last addition the temperature is raised to 280° C. and held until a test drop cooled on glass can be drawn out into about 5 filaments. When this point is reached it is taken from the fire and ladled until it has cooled down to 140° C. when 35 kgs. of turpentine are gradually added. The varnish is stored cool for at least a month. For use approximately equal parts of the varnish and the desired coloring matter are used and enough turpentine added to give a syrupy consistency. In order to obtain a good mixture, the whole is put through the mill 2 or 3 times. For coloring matter, besides yellow and red ochre, umber, green earth and paris blue the so-called pigment dyes are used which consist of aniline dyes precipitated on or combined with kaolin and the like. These dyes can be obtained in almost every shade.

To make the varnish for the enamel—100 kgs. of old linseed oil is heated to 180° C. and held at this temperature for 5 hours and it is important that the temperature does not exceed 180. Then the oil is allowed to cool to 150° C. and 2 kg. of manganese borate which has been rubbed to a paste with some oil, is gradually added. The temperature is then raised to 220° C. After 3 hours 1 kg. of cobalt oleate is added and the temperature raised to 260° C. and retained for 2 hours. This gives a lighter oil than the usual procedure. The prepared oil is allowed to settle and then poured carefully from any sediment into a clean container when it is stored in a cool place.

For automobile enamel 10 kgs. of the lightest zanzibar copal is melted as quickly as possible with constant stirring. With well regulated

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firing this can be accomplished in from 15 to 20 minutes, but the temperature of the copal should in no case exceed 350° C. When the mass is fluid and vapor no longer escapes from it, a drop placed on cold glass should be clear on cooling. Oil is then added to the melted copal, usually twice as much by weight, at a temperature of 100° C. only light linseed oil of good drying power and great elasticity, produced without a lead siccative should be used. The oil is stirred in well, small portions at a time. If the amount of oil is increased the elasticity is improved while the lustre is impaired. When all of the oil is stirred in about 10 to 12 parts of turpentine, heated to 50-60° C. on the water bath, is added for every 10 parts of the varnish. For use this is diluted further with turpentine.

Dull enamel is prepared as described for automobile enamel with the addition of beeswax. The more wax and turpentine added the duller will the enamel dry. It is essential that a pure beeswax be used since additions of japan wax, paraffin, ceresin and the like separate from the enamel on standing. G. W. S.

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OMA CARR

July 2, 1921.

It is with sorrow and deep regret we record the passing away of Mr. Oma Carr, who for more than twenty years has been prominent in the leather and allied industries, as chemist and engineer: Receiving his training at the University of Columbia, Washington, D. C. Mr. Carr began his career in the Bureau of Chemistry, U. S. Dept. of Agriculture under Dr. H. W. Wiley and, from the time the application of chemistry was recognised in this country as a coming factor in the manufacture of leather, he devoted his life to the promotion of the scientific and practical development of this phase of applied science.

Possessed of a mind exceptionally brilliant and original in conception, he in addition to his many attainments imbued all who knew him with his never failing spirit of progress. Genial and kindly to all, both in his professional and social life, it was a pleasure to be in his presence and for these qualities no less than his ability he will long be remenbered.

With his loss, at the age of man's greatest usefulness the gap in the roll of those who bore the brunt of early struggles to win recognition for this field of endeavor, is again widened.

Suffice it to say in life he did his full share, in death may he rest in peace. G. A. K.

COUNCIL MEETINGS

A meeting was held at the close of the annual convention at Atlantic City on June 11th, all the members of the Council being present. It was decided to hold a meeting of the Council in New York City as soon as the stenographer's report of the annual convention was ready for use. Permission was given to the trade papers to publish the addresses delivered at the convention by L. J. Robertson and George A. Kerr previous to their publication in our JOURNAL, this permission being granted on account of the papers being of general interest to the public.

A meeting of the Council was held in New York on July 15th, all of the members of the Council being present. Some of the back numbers of the JOURNAL being out of print it was decided that a letter should be written to the members of the Association

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stating what numbers we are especially in need of in the hope that in this way some of these numbers may be obtained from members who are not keeping a complete file of the JOURNALS. The numbers we are especially in need of are

1913—February, May, August and Index
1914—March
1915—January
1917—February and April

It was recommended that an effort be made this fall to obtain new advertisements for the JOURNAL and that members should cooperate in securing these advertisements as far as possible.

A change in the official method for the Analysis of Vegetable Tanned Leather proposed by R. W. Frey [see This JOUR., **16**, 228 (1921)] was not approved by the Council.

It was voted that the Procter-Searle method for the Determination of Free Sulphuric Acid in Leather as drawn up by J. B. Churchill [see Committee Report, This JOUR. **14**, 330 (1919)] be published in the JOURNAL and voted upon by the Association with a view to making it a provisional method.

F. H. Small was asked to draw up methods for the Sampling and Preparation of Leather for Analysis with a view to having the same adopted as part of the official method after the regular procedure.

G. W. Schultz was asked to submit to the Council the method of analysis for sulphonated oils recommended by the last committee with a view to having it adopted as a provisional method.

George D. McLaughlin, Director, was advised by the Council that committees would be formed to work on any subject which the Research Laboratory might think it advisable or practicable for the Association to work upon in that manner.

Committee work for 1921 and 1922 was recommended as follows and the following chairmen appointed:

Determination of Oils and Greases in Leather..W. K. Alsop
Determination of Sulphuric and Hydrochloric Acid in Leather.....A. W. Thomas
Determination of the Astringency and Penetrating Value of Tan Liquors.....R. O. Phillips
Determination of Moisture in Leather.....F. P. Veitch

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Chrome Leather Analysis.....L. Balderston
Determination of the Water Soluble of Leather.....
G. W. Schultz
Determination of the Sugar Content of Leather..J. S. Rogers
Determination of Sugar in Extracts.....J. S. Rogers
Direct Determination of the Plumping Power of Vegetable
Tanning Solutions.....V. J. Mlejnek
Color Determination of Vegetable Tanning Solutions.....
T. Blackadder
Alternative Filter Paper for Soluble Solids Filtration.....
L. M. Whitmore
Rapid Washing of Chromed Hide Power.....F. F. Marshall
Comparative Analysis.....H. C. Reed
Analysis of Synthetic Tanning Extracts.....T. A. Faust
Testing of Dyestuffs used on Leather
Determination of Epsom Salts in Leather.....R. W. Frey

EXTRACTION OF OIL AND GREASES FROM LEATHER*

Committee Report, 1921

By F. P. Veitch and I. D. Clarke

For several years both this association and the Society of Leather Trades Chemists have been engaged in the study of methods for determining oils and greases in leather and four papers bearing directly on the subject have been published since 1918.

Wilson and Kern[1] on comparing petroleum ether, carbon tetra-chloride ethyl ether and a mixture of equal parts of ethyl ether and carbon tetra-chloride in soxhlet extractors on greased (containing oxidized fats) vegetable tanned and on greased (sulphonated oil) chrome leather, found that carbon tetra-chloride extracted from 1½ per cent to 2 per cent more, ethyl ether about 2½ per cent more, and the mixture of carbon tetra-chloride and ethyl ether 2¾ per cent more than petroleum ether. No reference was made to the constituents of the extracts.

Levi and Orthmann[2] found that in soxhlet extractors a mixture of ethyl ether and carbon tetra-chloride extracted about 1½ per cent to 2+ per cent additional following extraction with

*Read at the 18th, Annual Meeting at Atlantic City, June 9, 1921.
[1]This Jour., 13, 138-41 (1918)
[2]This Jour., 13, 313-18 (1918)

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petroleum ether: that this mixture extracts 1.88 per cent from quebracho extract which had been previously washed with petroleum ether: that from a union sole leather from which petroleum ether extracted 2½ per cent the mixed solvent extracted 4.3 per cent, of which 0.94 per cent nearly a fourth was soluble in water, while from the water insoluble residue 0.91 per cent was dissolved by absolute alcohol. They found that chrome tanned leather fat liquored with soap, sod oil, and neat's-foot oil, and finished with blood albumen in the season, yielded from 1 per cent to 2 per cent more to the mixed solvent than to petroleum ether in fourteen hours, the extracts were colored and one contained 1.51 per cent of ash largely chromium oxide: that commercial blood albumen yielded 0.86 per cent to petroleum ether in fourteen hours, and 0.91 per cent in six hours on subsequent extraction in the mixed solvent.

In 1919, a committee of the American Leather Chemists' Association[3] compared five solvents: petroleum ether, carbon disulfide, carbon tetra-chloride, ethyl ether, and chloroform, on undyed and unfinished (crust) leathers, fat liquored or stuffed in six different ways. The samples were prepared by dividing a skin into sides, treating one side and leaving the other side untreated as a blank. The treatments were as follows: Nos. 1 and 2. Vegetable tanned kip fat liquored with moellon degras; Nos. 3 and 4, black chrome calfskin fat liquored with neat's-foot oil and soap; Nos. 5 and 6, chrome and vegetable-tanned hide stuffed with stearin and paraffin and a small amount of wool-grease; Nos. 7 and 8, vegetable-tanned hide fat liquored with sod oil and soap and stuffed with stearin; Nos. 9 and 10, chrome-tanned kip washed free from soluble mineral matter and then fat liquored with sulphated neat's-foot oil; Nos. 11 and 12, chrome and vegetable-tanned kip fat liquored with sod oil and soap and stuffed with stearin. The quantities of grease and soap taken up by the leathers was known only from the difference between the results obtained in the ungreased and on the greased sides. In every case chloroform was found to extract the largest quantity of material and petroleum ether the least. The results show further that from the ungreased duplicate sides of each sample chloroform extracted approximately 0.6 per cent

[3] This Jour., 14, 140 (1919).

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more than did petroleum ether, while from the sole leather samples the chloroform extract which gave positive tests for tannin, gave an average of 1 per cent more than the petroleum ether which gave no tannin reaction.

An attempt was made to determine the "absolute efficiency" of the solvents but the results were not conclusive. Chloroform, while it extracted more of the grease than did the other solvents, apparently did not, in some cases, extract all. Chloroform was, however, recommended, by a majority of the committee, for adoption as the official solvent istead of petroleum ether.

Levi[4], in discussing the report of the Committee, referred to some of his own work with finishing materials and dyes in which he obtained the following results:

From	Extracted by Petroleum ether	Chloroform
	%	%
Light blood albumen,	1.66	2.52
Casein,	.85	3.81
Shellac,	.13	101.32
Irish moss,	.06	.25
Gum tragacanth,	.02	.20
Egg albumen,	.04	.20
Alizerol brown,	.03	.16
Direct black R,	.05	.24
Acid green,	.02	.09
Bismark brown Y extra,	.03	.19
Orange A,	.07	.31
Waterless sod oil on wood pulp,	39.5	52.80

Veitch and Hunt[5] compared chloroform, ethyl ether and petroleum ether, by extracting with these solvents mixtures of eighteen typical leather stuffing oils and crushed quartz sand. Chloroform was in every case as good as or better than ethyl ether. Petroleum ether was in no case better than ethyl ether and had by far the lowest solvent action of any of the three, especially on oxidized oils and fats. They concluded that, "from these results it would appear that although chloroform is not 100 per cent efficient, it is by far the best solvent for oils and greases in general, and, the solubilities of other leather substances being eliminated or standardized, it would give more concordant and better results than either of the other two solvents."

[4]This Jour., 14, 500-1 (1919)
[5]This Jour., 14, 507 (1919)

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The report of the A. L. C. A. Committee for 1920 (read at the annual meeting but not published) dealt with the solubility of various tanning and leather finishing materials in petroleum ether and in chloroform.

Mr. Clark of the Bureau of Chemistry determined the quantities which are removed from a number of tanning materials by petroleum ether and also by chloroform and found from:—

	Dissolved by	
	Petroleum ether	Chloroform
	%	%
Chestnut wood extract,	.1	1.75
Solid hemlock extract,	.02	.82
Cube gambier,	.37	2.01
Solid quebracho extract,	.02	.07
Muskegon extract,	.01	1.04

chloroform extracted relatively much more than did petroleum ether, but tannin could not be detected by the gelatin salt test in any of the extracts.

Hunt found that of the commonly used finishing materials shellac alone was dissolved in any quantity by chloroform, which removed practically all the shellac from an intimate mixture of leather and shellac. To a sample of sole leather 8.7 per cent of shellac dissolved in alcohol was added and the whole dried at 60° F. To another portion of the same sole leather, Irish moss, dried blood, albumen and casein in water were added and dried at 60° F. The dried leather contained a total of 17.9 per cent of these finishing materials. The results obtained on these samples were as follows:

	Extracted by	
	Petroleum ether	Chloroform
	%	%
Ungreased sole leather,	2.5	3.5
" " " 8.7% of shellac,	1.8	10.0
" " " + 17.9% Irish moss by dried blood albumen and casein,	1.3	2.0
Shellac,		98.8
		100.6

Apparently both the shellac and the finishing materials coated the ground leather to such an extent that not as much was dissolved by ether solvent as from the untreated leather. Leather dyed with nigrosine yielded no color to the solvent after standing several days.

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The Dressing Leather Sub-committee of the Society of Leather Trades' Chemists[6], used six solvents: petroleum ether, ethyl ether, chloroform, carbon tetrachloride, carbon disulfide and benzene. The leathers used were a russet kip butt, a Memel kip side and three vegetable tanned sides fat liquored as follows: One with sulfonated cod oil, one with degras and the third with distilled Yorkshire grease and a little soap. A second series of extractions was also carried out using only the three solvents, chloroform, benzene and carbon disulfide. The leather used for this second series was prepared by treating portions of a vegetable tanned split as follows: (1) Untreated as a blank, (2) drummed for half an hour with equal weight of soap dissolved in warm water, then struck out and dried, (3) stuffed with linoleic acid, (4) fat liquored with one-fifth of its weight of soap and four-fifths of its weight of oleic acid, (5) soaked in warm water, struck out and weighed, then fat liquored with one-fourth of its weight of soap and an equal weight of oleic acid, (6) stuffed with oleic acid, (7) first extracted with chloroform (0.64 per cent removed), then stuffed with linoleic acid. Chloroform, benzine, B. P. 90° C., carbon tetrachloride, trichlorethylene and ethyl ether gave practically the same results on all samples and about 1 per cent more than petroleum ether, which gave a lighter colored grease.

In 1920 the same committee[7] worked with carbon disulfide, chloroform, carbon tetra-chloride, ethyl ether, petroleum ether, benzene B. P. under 90° C., and trichlorethylene. The four leathers used were fat liquored as follows: No. 1 with soft soap only, No. 2 with a mixture of castor oil and soft soap, No. 3 with sulfonated castor oil, and No. 4 with oleic acid, and soft soap.

The results were quite discordant but on the leather fat liquored with soft soap carbon bisulphide and trichlorethylene gave the highest results. Chloroform, benzene B. P. 90° C., ethyl ether gave closely agreeing results, while petroleum ether gave results about 1½ per cent lower. On the other samples chloroform, carbon disulphide, carbon tetrachloride, benzene, ethyl ether and trichlorethylene gave essentially the same results with a tendency for chloroform to give a little higher and darker colored extracts

[6] *J. Soc. L. T. Chem.*, 4, 7-10 (1920)
[7] *J. Soc. L. T. Chem.*, 4, 300-302 (1920)

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Petroleum ether extracted from 1 per cent to 2 per cent less than chloroform. The benzene extract was much lighter colored than the chloroform extract, but it was usually necessary to re-distill it in order to obtain a solvent with a boiling point under 90° C. The report states that carbon disulfide, carbon tetrachloride and ethyl ether are of use for special purposes but not suitable for recommendation as the official solvent. The committee state that although chloroform and benzene extract matter other than greases, they are probably better than petroleum ether which gives lower results than all other solvents. They propose that either chloroform or benzene be officially recognized as the solvent to be used in all determinations of grease in leather. If weight is attached to the color of the extract, then benzene is better than chloroform.

Committee Work During the Past Year. Soap alone or when mixed with sand is only partly extracted by petroleum ether or by chloroform: although more is extracted by chloroform than by petroleum ether. The fats of soaps are however more completely, if not entirely extracted from leather by both solvents, and it was deemed worth while to determine definitely the behavior to solvents of soap in leather and also to determine the cause of different behaviors to solvents of soap in the presence of leather and in the presence of non-reactive materials. Ivory soap was used in the experiments and the extractions were made in glass soxhlets using a paper thimble to hold the charge.

The time of extraction was varied both with soap alone and where the soap was mixed with sand and also cotton. For the sand soap mixture five grams of soap and 45 grams of sand were used and in one case they were mixed dry by stirring, while in the other case they were mixed by adding alcohol to dissolve the soap and then evaporating the alcohol with occasional stirring. For the soap cotton mixture, two grams of cotton were mixed with 5 gms. of soap. In one case they were mixed dry and in the other case water was added to dissolve the soap and then evaporated. The mixture was air dried, then dried in vacuo at 60° for 3 to 4 hrs. The results of the extractions of these various mixtures are given in Table III. The soap was only very slightly soluble in the solvents and this solubility was probably partially due to the presence of unsaponified fat. In two cases where the

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TABLE III.

Material extracted	Time of extraction	Chloroform: Soap extracted	Chloroform: Color of extract	Petroleum ether: Soap extracted	Petroleum ether: Color of extract
		%		%	
Soap	12	0.55	colorless oily	0.28	brown liquid
"	36	0.92	" "	0.30	" "
"	24	0.51	light yellow	0.23	light yellow
"	48	0.64	" "	0.27	" "
"	24	0.47	yellow		
"	48	0.57	"		
Soap and sand mixed dry	24	0.87	greenish oily	0.35	orange yellow solid
" " " " with alcohol	24	0.81	yellowish brown oily	0.34	cream colored solid
Soap and cotton mixed dry	24	0.59		0.26	
" " " " with water	24	1.60	solid-trace of yellow	0.50	V. light yellow liq.

NOTES: Results not corrected to moisture free basis. Moisture in soap was about 2 per cent.
No ash was found in any of the petroleum ether extracts and only 1 per cent to 1.5 per cent of neutral ash in the chloroform extracts.

TABLE IV.

EFFECT OF MOISTURE ON THE EXTRACTION OF SOAP FROM SAND BY CHLOROFORM.

Quantity of water added, cc.	%	Soap extracted in 24 hrs. %	Soap extracted in 48 hrs.	Ash on extract %	Color of extract
(1)					
0	0	0.70	——	0 neut.	U. P. yellow oily
0.25	0.5	0.73	——	1 "	" " "
0.50	1.0	1.09	——	1 alk.	light yellow
1.00	2.00	1.13	——	1.4 alk.	" "
0	0	0.84	1.00		U. light yellow oily
1	2	1.69	——	——	white cryst. solid
2	4	2.68	3.90	——	" " "
4	8	2.38	4.52	——	" " "

(1) Approx. 0.15 cc. present as moisture.

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soap was first extracted for 24 hours and the extraction then continued for 24 hours more only 0.1 per cent of material was extracted by chloroform, while less than 0.05 per cent was extracted by petroleum ether.

Since moisture would be expected to increase the solubility of soap, the effect of moisture was determined by adding different quantities of water to mixtures of 5 grams of Ivory soap and 45 grams of sand and extracting with chloroform. Results are given in Table IV.

There was no increase in the amount of soap extracted after adding 0.5 per cent and only a slight increase after adding 1 per cent of water. As the moisture increases, however, the percentage of grease increases quite decidedly so that with 4 per cent of moisture about 2.7 per cent of the actual soap present is dissolved about 1 per cent of which is alkaline ash. The soap is practically insoluble.

Mixtures of 5 grams of Ivory soap and 5 grams of sawed leather, which had previously been extracted with chloroform and petroleum ether, were also used in investigating the influence of moisture on extraction. One cc. of water was added and allowed to penetrate the dry mixture, which was then extracted for 24 hours. Petroleum ether extracted about 3 per cent of material containing 1 per cent of alkaline ash, while chloroform extracted 12.6 per cent of material containing 1.3 per cent of alkaline ash. The petroleum ether extract was a colorless solid while the chloroform extract was light brown in color. It seems clear from these results that the presence of moisture increases the solubility of soap in chloroform and petroleum ether. However, its effect is not great enough to explain the great solubility of soap from some soap and leather mixtures.

From a mixture of leather No. 14 and soap 32.9 per cent of the soap was extracted by chloroform and 6.7 per cent by petroleum ether (Table V). The extract with chloroform probably contained some tannin for it was brown in color but the petroleum ether extract was light yellow in color. The per cent of material extracted is calculated from the weight of the extract after drying

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TABLE V.

EXTRACTION OF MIXTURES OF SOAP AND LEATHER.

Material extd.	% Soap in mixture	Chloroform: % Of total extd.	Chloroform: % Of soap extd.	Chloroform: % Ash in ext.	Chloroform: Color of ext.	Petroleum ether: % Of total extd.	Petroleum ether: % Of soap extd.	Petroleum ether: % Of ash in ext.	Petroleum ether: Color of ext.
Leather No. 14	0	3.9	—	0	L. yellow liquid	3.7	—	0	L. greenish yellow liq.
" No. 14 and soap	50	19.0	32.9	1.5	L. brown liquid	5.3	6.7	1.5	L. yellow liquid
" 38255-A	0	1.9	—	0	brown oily solid	1.5	—	0	lard color
" " and soap	50	5.1	7.8		L. yellow solid	0.5	—	0	V. L. yellow solid
" 38255-B	0	2.1	—	—	V. L. brown solid	1.6	—		lard color
" " and soap	50	2.5	2.8	—	L. yellow semi-sol.	0.6	—	0	" "

Leathers 38255-A and B and the mixtures with soap were dried over night at 80° C. rel. humidity 65° before extraction. Leather No. 14 was air dried. The results are on the moisture free basis.

TABLE VI.

Material extracted	Chloroform: % Of total extd.	Chloroform: % Of soap extd.	Chloroform: Color of ext.	Petroleum ether: % Of total extd.	Petroleum ether: % Of soap extd.	Petroleum ether: Color of ext.
Tanned hide powder	0.21	——	yellowish brown solid	0.15	——	solid
Tanned hide powder and soap	13	25 to 30	light yellow semi-solid	5.7	11 to 13	L. yellow solid

Results on air dry basis.

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for six hours. The drying was continued for four hours longer, weighing every half hour, but constant weight was never reached. There was a loss of three or four milligrams per hour after ten hours drying and the extract became rather dark, so drying was discontinued. Similar results were obtained by extracting a mixture of tanned hide powder and soap. The hide powder was tanned by shaking with pure oak bark extract. · Five grams of the hide powder alone and a mixture of five grams each of the hide powder and Ivory soap were extracted for twenty-four hours. A fairly high percentage of material was extracted and again an extract was obtained which could not be dried to constant weight. The results given in Table VI are based on the weight of the extract after one hour drying, except where two figures are given, in which case the lower result is calculated from the weight of extract after drying twenty-eight hours. (See Table VI.)

The petroleum ether extract of the mixture contained 1 per cent of slightly alkaline ash and the chloroform extract 3 per cent of a strongly alkaline ash. Also during the extraction of the mixture with chloroform a clean jelly formed on the outside of the thimble so that the soap was probably carried over in a colloidal rather than in a true solution.

Very different results were obtained with leather No. 38,255, the amount of soap extracted from the mixtures with this leather being only slightly greater than the amount extracted with sand or cotton (Table V). This was a special leather which had been removed from the vats, dried in the crust and then sawed as for analysis. It therefore contained no added fats or finishing materials and gave on analysis the following:

Moisture	10.8%
Soluble solids	19.3%
Ash	0.36%
Hide substance	38.6%
Combined tannins and fat	31.0%
Sugars	0.24%

The leather No. 38,255-A was an untreated portion of this leather, while No. 38,255-B was prepared by extracting a portion

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of this leather with water at 50° C. by the usual method used for determining soluble solids, except that the extraction was carried on for six instead of three hours. The extracted material amounted to 22.3 per cent of the original weight. The per cent of hide substance in this leather was 52.9 per cent. It is to be noted (See Table V) that with both samples A and B less material was extracted by petroleum ether from the mixture of soap and leather than from the leather alone. The cause for this is not known.

Since it appeared that the presence of uncombined tannin, through reaction between the tannin and the soap, which sets free the fatty acid, is probably chiefly responsible for the extraction of soap from the mixtures of soap with leather No. 14 and with tanned hide powder, extractions were made of mixtures of soap, sand and tannic acid, in order to throw more light on this point. For one extraction the materials were mixed together dry, for another extraction alcohol was added, evaporated, and the mixture dried in vacuum at 70° C. for several hours, while for a third extraction they were mixed by adding water and then, after evaporating the water, drying in vacuum at 65° to 70° C. for ten hours. The extraction of this last mixture was made in duplicate. Ten grams of sand, two grams of tannic acid, and one gram of Ivory soap were used in each mixture. The results are given in Table VII.

The extraction of the material mixed by adding water was continued for 24 hours longer, but during this second 24 hour period, chloroform extracted only about 2.4 per cent and petroleum ether 0.4 per cent of material. During the chloroform extraction of the material mixed by adding water, in one case a clear and in the other a brown gel formed on the outside of the thimble just as was found in the extraction of mixtures of soap with leather No. 14 or with hide powder. Ash determinations were made on only two of the extracts. One per cent ash was found in the chloroform and 4.5 per cent ash in the petroleum ether extract. This gel formation and also the high solubility of the soap is therefore due to reactions between the uncombined tannic acid and the soap resulting in the decomposition of the soap and the setting free of the grease. It will be observed, however,

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TABLE VII.

EXTRACTION OF MIXTURES OF SOAP, SAND AND TANNIC ACID.

Material extracted	Chloroform			Petroleum ether		
	% Of total extd.	% Of soap extd.	Color of ext.	% Of total extd.	% Of soap extd.	Color of ext.
Tannic acid alone	0.06	——	white cryst.	0.02	——	——
Sand, soap and tannic acid mixed dry	4 to 5	50 to 64	light yellow	0.11	1.4	colorless
Sand, soap and tannic acid mixed with alcohol	5½ to 6½	71 to 86	dark	3 to 4	41 to 51	sl. dark
Sand, soap and tannic acid mixed with water	4.7 to 5.5	61 to 71	dark	5.1 to 5.8	65 to 76	brown
Sand, soap and tannic acid	4.8 to 5.7	62 to 73	dark brown	5.1 to 5.8	66 to 76	dark

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that even chloroform does not remove all the fats present either from leather or from mixtures of soap, sand and tannic acid. That some tannic acid or closely related compounds are dissolved in small quantities is indicated by these results and also by the fact that the extracted material continually lost weight on drying, which was shown by drying a mixture of 2 grams of tannic acid and one gram of Ivory soap, to which water had been added and then evaporated. After fifty hours drying, there was still a relatively large loss in weight, 10 to 20 milligrams per hour drying. Soap and tannic acid dried separately reached constant weight after a comparatively short time. Also the loss in weight of the mixture in a given time was more than the combined loss of the same amount of each material dried and weighed separately.

Some work was also done to determine the solubility of calcium and magnesium soaps and on the effect on fat extraction of the presence of calcium or magnesium salts in leather. Calcium and magnesium soaps of the fatty acids from Ivory soap were prepared by adding a solution of epsom salts and a solution of calcium chloride to warm solutions of Ivory soap. The precipitated soap was then washed free from sulfates or chlorides respectively and dried first in the air for several days, then in vacuum at about 80° C. for several hours. Five grams of these soaps were mixed with 45 grams of sand and extracted for 24 hours in a soxhlet. 80 per cent of the magnesium soap was extracted in chloroform and about 38 per cent was extracted or carried over by petroleum ether in 24 hours, apparently as a whole and without decomposition (Table VIII). The petroleum ether was rather milky during the first 48 hours, but was clear during the final 24 hour period. 48 per cent of the calcium soap was removed by chloroform but during the first two 24-hour extraction periods the solvent in the flask and around the thimble was very cloudy, so that the soap was carried over in a milky colloidal state rather than in a true solution. Calcium soap is practically insoluble in the petroleum ether used. Here too what soap was removed appeared to be removed without decomposition.

The solubility of several soaps at room temperature (27° to 30° C.) was also determined by adding an excess of the soap to about 100 cc. of the solvent in a glass bottle and allowing to stand for one or two weeks. Fifty cc. was then pipetted off using a

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TABLE VIII.

SOLUBILITY OF CALCIUM AND MAGNESIUM SOAPS.

	Chloroform				Petroleum ether			
Time of extn.	% Of total extd.	% Of soap extd.	Color of ext.	% Ash on ext.	% Of total extd.	% Of soap extd.	Color of ext.	% Ash on ext.
			CALCIUM "IVORY" SOAP					
1st 24 hrs.	4.8	48.2	transparent solid v. l. brown	15.9	0.3	3.0	white with tinge yellow	13.2
2nd 24 hrs.	1.6	16.4	white flaky	10.7	0.2	1.8	white cryst.	18.4
3rd 24 hrs.	0.35	3.55	——	13.3	0.06	0.6	——	16.8
Total 72 hrs.	6.8	68.2	——	ave. 13.3	0.56	5.4	——	ave. 16.1
			MAGNESIUM "IVORY" SOAP					
1st 24 hrs.	8.0	80.3	l. brown transparent solid	7.5	3.8	37.8	l. yellow solid	7.8
2nd 24 hrs.	0.2	1.8	lard color	3.7	0.5	5.35	colorless transp.	7.8
3rd 24 hrs.	0.2	1.6	——	1.8	0.1	1.1	——	6.2
Total 72 hrs.	8.4	83.7	——	ave. 4.3	4.4	44.25	——	ave. 7.3

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piece of filter paper over the end of the pipette to remove solids, and dried and weighed. Most of the solvent was then poured off, fresh solvent was added, and another 50 cc. portion removed after one or two weeks. The solubility is given in grams soluble in one liter.

	First portion	Second portion
Solubility of Ivory soap in petroleum ether	0.056	0.03
" " " " " chloroform	0.184	0.184

	First	Second	Third
Solubility of calcium "Ivory" in petr. ether	0.568	0 432	0.402

These results are probably high, due to a small amount of suspended matter being carried through the filter and also due to evaporation of the solvent when suction was applied to drain the solution into the pipette.

The calcium "Ivory" soap and chloroform formed a persistent emulsion when shaken together and there was no evidence of any separation into layers even after the solution had stood for a month.

Magnesium ivory soap was very soluble in both chloroform and petroleum ether. Enough soap was not prepared to saturate the quantity of solvent used, and when the solvent was evaporated from the petroleum ether solution by leaving the bottle unstoppered, the solution became more and more viscous until the solvent had entirely evaporated. The soap itself was a light brown amorphous substance.

Conclusion.

Dry Ivory soap is practically insoluble in chloroform and petroleum ether.

The presence of moisture in the material will increase the quantity of soap fats extracted by chloroform and by petroleum ether, but the effect of the quantity of moisture usually present in well air dried leather is small.

The presence of tannic acid probably by decomposing the soap and setting free the fatty acids, increases the solubility of soap fats very greatly but mostly in chloroform.

The grease extracts from materials containing uncombined tannic acid contain small quantities of tannic acid or related bodies and lose weight indefinitely on drying.

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Magnesium salts, added to leather, will lead to the extraction of the soap as a whole, if opportunity is given for the formation of magnesium soaps since the latter are very soluble both in chloroform and in petroleum ether.

Calcium soaps are extracted by chloroform in a colloidal state, but are practically insoluble in petroleum ether.

General Discussion by the Chairman of the Committee:— Committees of this Association have done three years' work and the committee of the Society of Leather Trades' Chemists has done two years' work all of which without exception shows that chloroform extracts more completely than does petroleum ether, certain oxydation products of oils and greases, waxes and similar materials: That small quantities of tanning or other materials are extracted by chloroform but not by petroleum ether: That the usual leather finishing materials not of a fatty or waxy nature used on leather are not dissolved in any material quantity: That there is no evidence that dyes are dissolved in sufficient quantity to materially affect the results of the grease determinations.

The work done the past year indicates very positively that chloroform is a much better solvent for the fats present in soap than is petroleum ether, but that all the soap fats are probably not removed by chloroform when the extraction is made as usual. This work also brings in question the results obtained on leather containing soaps which are extracted without first removing the fats and soaps, since part of the soap will be included in the fat determinations and also in the determination of water solubles. More work needs to be done on the solubility of soaps from different greases before we will know how serious this error may be.

Recommendations.

It is believed that enough has now been done both here and abroad to show that chloroform is probably the most reliable solvent for grease in leather, and it is accordingly recommended that chloroform be substituted in the methods for petroleum ether as the grease solvent. It is also recommended that work be continued on the solubility of various soaps in solvents and upon a method, probably first breaking up the soap by heating the leather with an acid, for the extraction of the total soap greases in leather.

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Discussion.

Following the presentation of the committee report on the extraction of oil and grease from leather the followng discussion took place.

President Small: The possibility that the amount of material extracted by the solvent is dependent in part on the amount of moisture in the leather is a point that came up in connection with the work of the Committee on the Sampling and Preparation of Leather for Analysis. Considerable time was devoted to this subject in the Laboratory at Ridgway and before throwing the question open to general discussion I would like to have Mr. Alsop or Mr. Schultz tell us a bit about the work that they did in extracting leather with chloroform and the effect of the moisture in the leather on the extraction.

Mr. Schultz: In the work of the Committee on Preparation and Sampling of Leather, we ran chloroform extractions on a large number of samples after extracting with petroleum ether and we found that the additional amount extracted by chloroform varied very erratically for samples taken from different parts of the leather, the amount varied from three tenths of a per cent to two and one half per cent. That leather was oiled with a mixture of mineral and fish oil.

After distilling off the chloroform and evaporating to dryness it was found that this extract was no longer completely soluble in chloroform, only a very small proportion of it was soluble, but we found that it was completely soluble in alcohol. That portion of the extract that was insoluble in chloroform was found to be soluble in water also, which certainly did not point to the presence of oxidized fats.

We thought at first that the additional extractive matter was due to the presence of alcohol in the chloroform, but after carefully purifying our chloroform we found that the same results were obtained. Further investigation showed that it was the moisture content of the leather which influenced the amount of extract that was removed with chloroform. The higher the moisture content of the leather sample, the more was removed by an extraction with chloroform. The petroleum ether extract remained the same in all cases.

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By drying the samples of leather before extracting, we thought that we might eliminate the influence of the water on the extraction with chloroform which was found to be true but we also found that there was evidently a considerable percentage of the fat lost in drying the sample as our petroleum ether extracts were low. Nevertheless, the petroleum ether extract in that case and the chloroform extract practically coincided. There was a very small difference between the two extractions for the samples we worked with.

It is natural to assume that petroleum ether will not remove oxidized fats and the like but under the condition of a grease extraction is the assumption likely to prove correct? The Committee on Dressing Leather of the S. L. T. C. found that petroleum ether removed chrome soap from a sample of chrome leather. It was also demonstrated by the Committee on Chrome Leather Analysis of the S. L. T. C. that all of the sulpher present in two-bath chrome leathers was completely extracted with petroleum ether. As we know, sulphur and chrome soap is not usually considered soluble in petroleum ether.

After we have considered all that has been said and done on the question of fat extraction, it points to the whole question as being rather complicated and I don't think that anything should be done hastily in the matter of adopting a solvent until a complete and careful investigation of every phase of the question has been made.

PRESIDENT SMALL: This rather pronounced effect that moisture in the leather has on the amount of material extracted by chloroform certainly must have careful consideration in discussing the possible adoption of chloroform as the solvent for the extraction of grease.

MR. VEITCH: In connection with that matter of the effect of moisture on the extraction, I find here in the text an experiment with a mixture of soap and leather to which about 10 per cent of moisture was added and then extracted for twenty-four hours. This material contained 50 per cent of soap. The extract with petroleum ether was 3 per cent, containing 1 per cent of alkaline ash. Chloroform extracted 12.6 per cent, containing 1.3 per cent of ash.

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With the sand-soap mixtures, to which I referred, with only the natural water of a thoroughly air-dried soap-sand mixture, 0.7 per cent containing no ash, was extracted by chloroform; with ½ per cent of added moisture 0.72, with 1 per cent of added water the extract rose to 1 per cent and contained about 1 per cent of alkaline ash; 2 per cent moisture, 1.3 per cent; with no added moisture, 0.84 per cent; again 2 per cent added water, 1.69 per cent of extract; with 4 per cent, 2. 68 per cent of extract; with 8 per cent of water, 2.38 per cent of extract. Here we had ash always present. Of course this sand-soap mixture and sand-oil mixture behaves differently from a leather-grease mixture and we cannot draw very many conclusions from that, except as showing absolute solubility. We would expect more effect from the presence of moisture in leather than we would on the sand-soap mixture.

MR. ORTHMANN: Mr. Chairman, I have had a little experience with using chloroform I find that my results are practically identical to what Mr. Schultz reported. I would suggest that we let petroleum ether still remain the official extractive. I cannot see why we should change at the present time to chloroform.

MR. FAUST: Mr. Chairman, there is one development, which has taken place during the past year which is going to effect the use of petroleum ether a little, although it may not be so very serious, and that is the fact that they are using more sulfonated oil in oiling leather and petroleum ether won't extract the oil well.

MR. ORTHMANN: I think you will find all of the sulfonated oils more or less soluble in petroleum ether, more than in chloroform. The reason I believe we should adhere to one definite solvent is because it would necessitate using a different solvent for different leathers, depending on the kind of materials these leathers were fat liquored with.

MR. ROGERS: We have a great deal of data obtained by the use of petroleum ether and the results of the Committees for the last two or three years have given us some idea about how efficiently petroleum ether will remove the fats. In those cases where soaps and waxes difficulty soluble in petroleum ether are present, and their extraction is desired, it would seem reasonable to follow the regular extraction with petroleum ether by an extraction with chloroform. If we are analyzing leathers in which we know that the oils and fats are soluble in petroleum ether, that

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extraction will be sufficient; but in cases where they contain oils or fats which we know are not extracted by petroleum ether but which can be extracted by chloroform, a subsequent extraction with chloroform can be made, bearing in mind the other materials that are taken out with chloroform and giving these due consideration when the results are interpreted.

The American Chemical Society Committee on the analysis of fats and oils in their method for the determination of insoluble impurities use kerosene followed by cold petroleum ether, stating that "petroleum ether cold or only slightly warm is not a good fat or metallic soap solvent, whereas, kerosene dissolves these substances readily."

DR. BUMCKE: No matter what solvent you take, you cannot accept the extract as pure oil or fat, because according to its condition you will always dissolve more or less of the soap, especially if the oil contains much free fatty acids which creates a solvent for the soap, and consequently you must afterward determine the ash in the extract and then figure out how much soap you have contained in it and deduct it from the grease.

DR. LEVI: Mr. Chairman, I would suggest before the Association adopts the method of using chloroform or petroleum ether, that the work of the Committee be continued for another year, using the different synthetic solvents that are on the market to-day, such as the acetylene dichloride and tetrachloride, and the like; in the reports next year see what results they will get by the use of these materials. I don't think the Association should adopt any method at the present time until the experiments have been tried with all the solvents easily obtained at a reasonable cost.

MR. VEITCH: Practically all of them have been tried. The English Committee especially used a great many of those solvents and their conclusion is that either chloroform or benzene is to be preferred.

RAPID WASHING OF CHROMED HIDE POWDER *

By R. W. Frey and I. D. Clarke

It will probably be recalled that in 1912 a committee of the A. L. C. A. was formed to revise the methods of tannin analysis.

*Read at the 18th Annual Meeting at Atlantic City, June 11, 1921.

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Among the changes proposed was one for washing the chromed hide powder for non-tannins. It was pointed out by the committee that the old method which simply specified washing by squeezing through linen until the wash water gave no precipitate with barium chloride was too indefinite for it is "practically impossible to wash until no test for sulphates is obtained and furthermore "too much washing has the effect of getting the powder in a condition in which it will not detannize properly." With the idea of more specific directions for better concordance, the present official method defining the amount of wash water, the number of washings, and the time was proposed. In the report of a later committee appointed to test these proposed official methods the only comments concerning the washing of the chromed hide powder were that "the proposed requirements are good." No comparative work on the washing of the powder was done.

There is little doubt that the changes proposed by the committee were steps in the proper direction. The following results however will show that the time of washing was unnecessarily prolonged.

The official method specifies in part as follows: "Squeeze and wash, by digesting with four successive portions of distilled water, each portion equal in amount to 15 times the weight of the air dry powder taken. Each digestion shall last 15 minutes * * * *."

Strict adherence to this method requires a total time of about 1 hour and 10 minutes and in addition necessitates working on a schedule. It will also, no doubt, be admitted by many that too often in a busy laboratory the schedule becomes sadly disarranged and the washing may be done in ¾ of an hour or may extend over 1½ hours.

There has been used in this laboratory, at times, a quick method of washing which might be considered a compromise between the old method and the present official one. The chromed hide powder is poured into a bag of linen or other suitable cloth and washed by draining. The cloth may be conveniently supported over a large ring, clamped on a ring stand or a large tripod using clothes-pin clamps for readily fastening and detaching. The same

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number of washings and the same volumes of water as are specified in the official method are used, but as soon as the water from each washing has practically run through, that is, subsided to the level of the powder in the bag, the powder is squeezed as usual. In this way the washing is almost continuous and can be done in 15 to 20 minutes, a saving of time which is desirable, especially on occasions when the quick chroming is used or when a quick method of analysis is employed.

A direct comparison of this method with the official method has been made, the results of which are given in Table I. For each sample, two liters of official strength were made up and the determinations were conducted on aliquots of the solution. With the exception of the total solids and some of the blanks, all of the figures are averages from closely agreeing duplicates. The work was done on three different dates using the official hide powder, Lot No. 1.

TABLE I. Comparison of Official and Rapid Washing of Chromed Hide Powder.

L. & P. No.	Analysis dated	Description of extract.	Per cent total solids.	Per cent soluble solids.	Per cent Non tannins.		Per cent Tannins.	
					Official	Rapid	Official	Rapid
38899	5-6-21	Sumac	42.83	41.18	18.42	18.32	22.76	22.86
38900	5-6-21	Chestnut wood	44.78	42.90	14.37	14.31	28.53	28.59
38901	5-9-21	Hemlock bark	45.63	41.70	13.35	13.36	28.35	28.34
38902	5-9-21	Oak bark	46.91	43.83	17.40	17.32	26.43	26.51
38903	5-9-21	Powd. chestnut wood	93.54	90.95	30.35	30.38	60.61	69.58
38904	5-12-21	Larch.	50.38	44.60	19.36	19.32	25.24	25.28
38906	5-12-21	Solid quebracho	80.02	73.15	5.36	5.31	67.79	67.84
38907	5-12-21	Liquid quebracho	50.30	49.36	14.70	14.76	34.66	34.60

Used 46.5 gms. wet chromed hide powd. for 200 cc. solution.

(For analyses dated	5-6-21	5-9-21	5-12-21
(% Moisture—wet chromed hide powd.—official wash	73.76	72.69	72.10
(% Moisture—wet chromed hide powd.—quick wash	72.97	72.53	72.46
(mgs. blank on H_2O + cloth + kaolin + paper—100 cc.	3.3	3.0	3.0
(mgs. blank on H_2O + cloth + kaolin + paper + hide powd. (official)—100 cc.	6.0	4.7	3.5
(mgs. blank on H_2O + cloth + kaolin + paper + hide powd. (quick)—100 cc.	5.1	4.7	3.8

The data show conclusively that the rapid washing of the chromed hide powder gives as good results as does the official method. Prolonged contact of the hide powder and water offers no advantage and under some conditions, such as hot weather, it

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is not difficult to conceive of a detrimental effect. If such effect does occur the varying time of washing certainly would not make for agreeing results.

It is proposed that the rapid washing be adopted as official.

LEATHER AND PAPER LABORATORY,
BUREAU OF CHEMISTRY, WASHINGTON, D. C.

THE DETERMINATION OF GLUCOSE IN LEATHER*

Committee Report 1921

J. S. Rogers, Chairman

After a survey of the results obtained by last years committee[1] it was decided that the work this year should be directed toward the development of a procedure by which the lead could be completely removed from the clarified solution. With this end in view, the following materials have been tried out; Na_2CO_3, Na_2SO_4, and Na_2SO_4 followed by H_2S water. None of these materials seemed satisfactory. Some did not remove the lead completely and others were very disagreeable to use in a regular laboratory procedure.

Lead phosphate, $Pb_3(PO_4)_2$ is precipitated from a solution of lead acetate by di-sodium acid phosphate, Na_2HPO_4, and lead phosphate is practically insoluble in acetic acid. The solubility of lead phosphate in 100 parts of water at 20° C. is 0.000014, while the solubility of lead oxalate is 0.00016 at 18° C., and the solubility of lead sulphide is 0.0001.

It was therefore decided to try sodium phosphate for the removal of lead. Preliminary experiments gave some promise of success, and work was outlined and samples sent out to the committee. The sample of leather used was the same as that used by last year's committee[1]. It was an oak-chestnut tanned leather to which no sugar or salts had been added. The dextrose was a sample taken from a bottle of Merck's highest purity dextrose and showed 99.6 per cent dextrose by analysis.

Directions and samples were sent to R. W. Frey, Leather and Paper Laboratory, Bureau of Chemistry, Washington, D. C., and to L. A. Cuthbert, Elk Tanninng Co., Ridgway, Pa.

*Read at the 18th Annual Meeting at Atlantic City, June 9, 1921.
[1] *J. A. L. C. A.*, Vol. 15, 1920, p. 411.

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The directions were as follows:—

I. Extract two 30 gram portions of the leather sample sent out, by regular procedure, make each extract to 2000 cc. then mix so as to give one solution of a volume of 4000 cc.

II. Prepare five dry one liter graduated flasks. Number them one to five. In No. 1 place 1.2048 grams of the Merck's dextrose sent out, fill and make to volume with distilled water and mix. In No. 2 place 900-950 cc. of the leather extract. In No. 3 place 1.2048 grams of dextrose and fill and make to volume with the prepared leather extract and mix. In No. 4 place 1.05 grams $MgSO_4 7H_2O$, fill and make to volume with the prepared leather extract and mix. In No. 5 place 1.2048 grams of dextrose and 1.05 grams $MgSO_4 7H_2O$, fill and make to volume with the prepared leather extract and mix.

III. Treat the above five solutions in duplicate as follows: (In order to obtain the first filtrate in less time it has been decided to double the amount of solution generally used; thus starting with 400 cc.). Place 400 cc. of leather extract in a flask and add 50 cc. of saturated lead acetate solution, mix and filter. Pipette 180 cc. of the clear filtrate and add 30 cc. of warm (30-35° C.) 50 per cent Na_2HPO_4 solution, mix and filter, returning until clear. Pipette 175 cc. of the filtrate into an Erlenmyer flask, add 5 cc. concentrated HCl, boil for 1½ hours under reflux condenser, disconnect from condenser and continue boiling for ½ hour, cool, neutralize with a concentrated solution of NaOH making alkaline to litmus paper and adding about ½ cc. in excess, cool if necessary make to 200 cc., mix, filter, and determine sugar by regular procedure, making duplicate reductions.

Special solutions required:

Caustic Soda Solution: Concentrated NaOH nearly saturated.

Sodium Phosphate Solution: Fifty per cent $Na_2HPO_4 12H_2O$. Dissolve hot and make to volume at about 35° C. This solution will crystalize out on cooling and must be warmed to about 40° C. to dissolve and cooled to 30-35° C. before using.

Results obtained according to these directions are given in Table I.

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TABLE I.
RESULTS OBTAINED WHEN LEAD IS REMOVED BY Na_2HPO_4

	Water solution 8% dextrose	Leather extract alone	Leather extract + 8% dextrose	Leather extract + 7% epsom salts	Leather extract + 8% dextrose + 7% epsom salts
L. A. Cuthbert *	8.01	.63	8.56	.61	8.75
Elk Tanning Co.	7.90	.63	8.73	.57	8.86
	8.01	.68	8.52	.80	8.73
	7.98	.70	8.48	.68	8.81
Avg. % dextrose found	7.97	.66	8.58	.67	8.79
% " added	8.00	.00	8.00	.00	8.00
% ± Error deducting blank	— .03		— .07		+ .12
J. S. Rogers, Laboratory	8.11	.68	8.92	.92	8.77
International Shoe Co.	8.02	.78	8.81	.86	8.62
	8.22	.70	8.84	.70	8.94
	8.11	.82	8.85	.54	8.76
Avg. % dextrose found	8.12	.74	8.86	.75	8.77
% " added	8.00	.00	8.00	.00	8.00
% ± Error deducting blank	+ .12		+ .12		+ .02
Maximum individual results	8.22	.82	8.92	.92	8.94
Minimum " "	7.90	.63	8.52	.54	8.62
Greatest difference	.32	.19	.40	.38	.32
Gen. avg. % dextrose found	8.05	.70	8.72	.71	8.78
% Dextrose added	8.00		8.00		8.00
Avg. ± Error deducting blank	+ .05		+ 02		+ .07

*Used Aliquot =.4731 grams sample instead of .5 grams called for in directions.

If the general averages alone were to be considered it would appear that the use of Na_2HPO_4 for the removal of lead was very satisfactory. It is found however upon closer examination that there is considerable variation in the duplicates and in the results obtained by the two operators.

The average results obtained this year are compared below with those of Table No. 2 of last year's Committee Report[2] in which neutralization was made by NaOH and in which the lead had been incompletely removed by potassium oxalate.

From this comparison it will be noted that the average errors this year are all slightly positive, whereas, those last year were negative with one exception and in this case the greatest difference was .92 per cent. The negative errors last year were attributed to the action of lead plumbite. This year when the lead was more completely removed by use of Na_2HPO_4 we found the average error was slightly positive. The greatest differences this year were less than for last year.

[2] *J. A. L. C. A.*, Vol. 15, 1920, p. 410.

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TABLE II.

		Last year.	This year.
Water solution +8% dextrose	Avg. % dextrose found	7.88%	8.05%
	Avg. % ± error	— .12%	+ .05%
	Greatest difference	.40%	.32%
Leather extract +8% dextrose	Avg. % dextrose found	8.63%	8.72%
	Avg. % dextrose from leather extract	.96%	.70%
	Avg. % added dextrose found	7.67%	8.02%
	Avg. % + error	— .33%	+ .02%
	Greatest difference	.58%	.40%
Leather extract +8% dextrose +7% epsom salts	Avg. % dextrose found	9.00%	8.78%
	Avg. % dextrose from leather extract	.95%	.71%
	Avg. % added dextrose found	8.05%	8.07%
	Avg. % ± error	+ .05%	+ .07%
	Greatest difference	.92%	.32%

The results indicate that this procedure is successful in removing the lead and thus permits the use of NaOH for neutralization after hydrolysis. This being the case, it will be possible to use this procedure alike upon leathers with and without epsom salts present. In this respect it would seem that the committee has made decided progress this year.

The Chairman does not feel justified, from the few results thus far obtained, in recommending this modified procedure for adoption as an official method. It is felt, however, that it most certainly merits further careful study. Better concordance in results should be obtained and the method should be tried out by a large Committee. As a suggestion to next year's Committee, it is recommended that the following procedure be investigated: Place 200 cc. of leather extract of analytical strength in a 500 cc. flask, add 25 cc. of the saturated solution of normal lead acetate, shake frequently (10-15 minutes), and filter on 15 cm. plaited filter. (The funnels and beakers must be kept covered to prevent evaporation). Allow to drain until 190 cc. have been collected, pipette 180 cc. of the filtrate and add 30 cc. of 50 per cent Na_2HPO_4 which has been warmed to 30-35° C. Mix frequently for 15 minutes and filter, returning until clear. Collect 180 cc. Pipette 175 cc. of this filtrate into a 600 cc. Erlenmeyer flask, add 5 cc. of concentrated HCl and boil under reflux condenser for 2 hours. Cool, neutralize with concentrated NaOH using one drop of phenolphthalein, add ½ cc. in excess, cool to room temperature if necessary, transfer to a 200 cc. graduated

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flask and make to volume. Filter through a double filter. Determine dextrose in this solution immediately by the regular procedure.

SOME APPLICATIONS OF SYNTHETIC TANNING MATERIALS*

By J. B. Hill and G. W. Merryman

The modern trend in tanning toward which a great deal of effort is being expended is to cut down the time of tannage without impairing the quality of the leather. The present and from all indications the future economical situation demands a quicker turnover of the capital as represented in the hides in process.

To cut down the time of tannage it is necessary to increase the rate of diffusion of the extract into the hide substance. The penetration of the tanning material into the hide involves both a chemical and physical action. The rate of penetration besides being dependent upon the physical condition of the hide is also in a large measure dependent upon the concentration of the tanning bath. As is well known, however, too strong a liquor at the start will give a heavy surface tannage known as "case hardening" through which it is then difficult to drive the vegetable materials. Then the unequal tension set up between the tanned surface fibres and the untanned fibres in the center causes the drawing of the grain and gives a poor quality leather. For this reason the early tannage of the heavier skins is done in rather weak liquors. It is this slow building up or tannage of the hide which is the great consumer of time. Therefore it is conceded that any agent which will increase this rate of diffusion so that more concentrated liquors can be used and still get an even, uniform tannage throughout will be of value in the tannery.

In late years the time has been materially cut down by mechanical means such as improved rocker systems, drums and other mechanical and physical means of forcing the tanning liquors more rapidly into the hide. The mechanical handling and driving of the tannins will still continue to be improved.

In looking at the problem from the chemical viewpoint, it can be seen that any agent which will permit the use of more con-

*Read at the 18th Annual Meeting at Atlantic City, June 10, 1921.

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centrated baths so as to increase this rate of diffusion without the usual ill effects will answer a very great need and go a long way toward cutting down the time of tannage. This is the value of synthetic tannins and it can safely be predicted that in the future they will play an even more important part in the tannery than at present.

The exact nature and function of synthetic tannins does not seem to be clearly understood at present. At the very mention of the word "synthetic" as applied to tannins, most tanners at once become skeptical. This attitude is in a large part due to the negative results which some tanners have obtained and to the varied character of the many syntans now on the market. Of all the syntans available there seem to be no two alike even though the uses are the same.

The failures of the syntans in some tanneries may have been due to either the quality of the syntan or to its method of application. Being acid in character, their use has to be controlled very carefully. The acidity or hydrogen ion concentration is one of the most important factors in tanning and if allowed to become too high considerable harm results. A proper control of the use of the right acids is a decided advantage. In most cases where leather had been harmed by the use of syntans it has been due to the acid concentration becoming too high. In other cases the poor results have been due to an incorrect ratio of the synthetic product to the vegetable tannin in the yard or to a poor quality syntan, having for example a high content of free sulphuric acid.

The quality of the syntans is a very important factor in the results to be obtained. The purity and nature of the materials from which they are made and the skill in making them all affect their quality. Being for the most part sulphonation products they contain some free sulphuric acid. High grade syntans will contain very little free sulphuric acid and in some cases none or only a trace. They should furthermore be uniform in quality. Unfortunately it is very easy to imitate a high grade syntan since any acid tends to act more or less as a driver of vegetable tanning materials and as a bleach. Therefore it can readily be seen that almost any mixture with a little free acid present will show some of the properties of a synthetic material.

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So-called "synthetic tanning materials" may be divided into two main classes; first, those which act as real tannins and second, those which do not. A tannin is generally defined as one of those organic substances which has the property of converting hide substance into the imputrescable and permanent product known as leather. The two classes of syntans may be distinguished from each other by their ability or inability to perform this function. The first class may be used alone as a tanning bath and will give a true leather. The second class can be used only in conjunction with real tannins as aids to the tanning. The classification is unfortunately confused by the presence on the market of syntans which are a mixture of a synthetic non-tannin, *i. e.*, a substance of the second class, with a true vegetable or mineral tanning material. Such compounds do not properly belong to the first class, not being synthetic tanning materials in the narrowest sense of the word, and are therefore not included when this class is mentioned in this discussion. The first class includes principally the groups of compounds generally similar in a chemical way to the German product Neradol D, this particular product being a condensation product of cresol-sulphonic acid with formaldehyde.

The actual tanning value of a synthetic tanning material cannot be determined in the laboratory by the hide powder method of analysis, since these compounds are always acid in nature. In the test the acid is absorbed by the hide powder giving an apparent tanning value which is high, due to the fact that the absorption of the acids not strictly tannins is reversible, the compound being washed out with water. Pure sulphuric acid, for example, while being without tanning value, will show a "tannin" content by the official hide powder method. Much better and probably fairly accurate results may be obtained on the tannin content of these materials by other methods, such as that recently outlined by Wilson and Kern. Such a method shows the true "tannins" which combine and cannot be washed out. Further laboratory analysis shows the total solids, soluble solids, total acidity and possibly the amount of free sulphuric acid present. Color tests on sheep skins will show the color the syntans will impart to the leather when used alone or in blends with the vegetable materials. Even from the most complete laboratory

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analysis however it is hardly possible to judge the real value of a syntan when used in the tannery. The reliability of the manufacturer and the actual tannery results will have to serve to some extent as an index of the purity and of the real tanning value of the syntans.

Synthetic extracts are strictly not substitutes for, or imitations of, the natural products. Their use and general properties have been known for some time but their development has been rather slow. While this has been due to some extent to the difficulties which some tanners have gotten into in using them, it is in a large measure due to the veil of secrecy which has surrounded this type of tanning material and the resulting feeling with the tanners that something was being "slipped over on them." A little more enlightenment and a freer discussion of them between the manufacturer and tanner will create a greater feeling of confidence and hasten their development.

Let us discuss first the application of syntans of the first class, that is compounds which possess in themselves a real tanning value. Those compounds can be used alone to completely replace vegetable tanning materials. Their use however in this way is not very satisfactory on account of the fact that in general they lack filling power and give therefore a light flat leather of high tensile strength but little body. Their principal application is in light leathers in conjunction with vegetable extracts. Due to the many variable factors entering in in individual tanneries no fixed set of rules can be laid down for their use; the strength and proportion used and the exact method of working must be adapted to the particular leather and the particular tanning practice. The general advantages however which are claimed for this type of syntans used in this way are as follows:

1. They act as an accelerator or driver of the vegetable tans, permitting the use of stronger liquors at the start, thus cutting down the time to tan. This gives a better and quicker penetration of the tanning material into the hide without the usual ill effects.

2. They will give a tougher and smoother grained piece of leather with a better break.

3. They do actually tan the hide so that a saving can be effected in the amount of vegetable materials used. In some

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cases it has been found that one pound of the syntan will replace two pounds of the vegetable extract.

4. They will serve as a clarifier of the vegetable extracts increasing the solubility of the non-tans and converting them into tannins. This increases the efficiency of the tanning liquors.

5. They have a decided bleaching effect and therefore tend to replace the sulphite or other similar products. Being acid in character they do not strip the tannage as do the weak alkalies generally used. They impart a bright clean looking and very desirable color to the leather. This is of especial advantage in the first tanning liquor which largely determines the color of the finished leather.

There appears to be a further use for this class of syntans as a deliming and plumping agent. Used in this way they show the advantage over the usual acids of givinig a preliminary tannage and thereby preparing the hides better for the real tannage, in that the hides can be placed in stronger tanning baths and the tannage made to proceed much more rapidly.

Synthetic Tans for Upholstery or Split Leather

One of the most successful applications of the syntans thus far has been in the upholstery or split cowhide leather. They have chiefly been used as a preliminary tannage before placing the hides in the yard or rockers and in the retanning of the "splits."

As a preliminary tannage in a paddle wheel or pit either alone or in conjunction with the spent liquors from the yard, they give the advantage of starting the tannage in an even uniform manner and with a very rapid penetration. The hide is plumped or the fibres so opened up that when placed in the tanning baths the tannage is much more rapid. An examination of the hide after this preliminary tannage shows it to be of a very light uniform color, with a smooth even grain and a good penetration of the extract into the hide. This utilization of extracts from the yard gives an additional tanning value from them which would not be obtainable otherwise. This operation if done in a paddle wheel would require not more than a day. In a drum the time would be much less. In no case would it be necessary to use more syntan than 5 per cent by weight of the pack. By this treatment

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the hide can be split more readily and there will be fewer raw spots in the "splits."

It is possible to start the tanning in a drum with the syntan and a small percentage of fresh extract added at intervals. At the end of six to eight hours drumming the liquors are exhausted and the tannage has progressed far enough that the yard or rockers can be eliminated and the hide placed directly in a rather strong vegetable extract in the paddle tub. After a day or two of paddling the hide can be split and finished as usual. If the drum tanning is carried far enough it is possible to split directly from the drum. With sufficient syntans the hides can be plumped so as to get a very good yield in splits.

In the retanning of the splits certain syntans give excellent results even when used alone. They give a penetration which is not obtainable with the extracts themselves. They will completely tan the raw spots without giving any additional body to the leather. The leather will be firm but soft and pliable and of a very light color. They remove all spots and stains, so that it will not be necessary to give the leather a special treatment for this purpose as is so often necessary. The fibres of a coarse hide are knitted closer together and strength is added to the leather. Giving additional strength is an especially desirable feature of the syntan for this type of leather.

The amount required for the retanning varies with the syntan. When used alone the retanning is done in a 20 to 30° Bark bath. In conjunction with the vegetable extracts, there is generally added ½ to 1 lb. of the syntan per split. Practice will show that the syntan will replace some of the vegetable extract so that a saving in extracts can be effected. The time required for retanning is materially shortened.

Synthetic Tannins for Tanning Sole Leather

The syntans as applied to the heavy leather industry for the tanning of sole leather can be used to advantage at five different stages of the process as follows:

1. They can be used in deliming or as a permanent plumping agent and powerful aid to the rapid penetration of the tanning material.

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2. They can be added directly to the rockers where they act as a plumping agent and help the penetration.

3. They serve as a driver of the concentrated tanning extracts in the retanning or extracting wheel.

4. They are used as a bleach and filler with Spruce Extract.

5. They are added to the oil and dope mixture to give a better penetration and to hold the color.

When used as a deliming or plumping agent, the stock after unhairing and washing in clean water is run in the paddle wheel with the syntan for thirty to forty minutes. The strength of the deliming bath will depend upon the acidity of the syntan used. When the hides have attained the desired degree of plumpness they are hung in the rockers as usual. Compared to lactic, acetic, formic and other plumping acids they give a milder grain and a plumper leather.

They are used in the rockers by adding to the middle rocker from day to day sufficient syntan to maintain the desired acidity. This acidity will vary for different yards from a few hundredths to one-tenth per cent calculated as sulphuric acid. The acidity at this point must be very carefully controlled by chemical analysis so as to avoid an over concentration. In a rocker system ranging from 20 to 40° Bark. the stock is practically struck through in about 18 days. It will be observed that the hide is very plump and full, particularly so in the offal (shoulders and bellies).

For use as a fixing agent and driver of the heavy tanning liquids in the retanning wheel, the syntans are added directly to the concentrated extracts. The usual procedure is then followed as to the addition of the extracts, drumming, the time of which is shortened, and subsequent treatment if any in the tempering baths. The addition of the syntans to the heavy extracts will increase the solubility of the solids and give them a much better penetration and weight producing power. It will be especially observed that the leather when removed from the wheel will be much brighter and cleaner in appearance. They have a decided bleaching effect at this point.

Certain of the syntans in combination with Spruce Extract give excellent results as a bleach and filler. The leather is usually taken at the point where it is to be given the soda-acid bleach

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and, after wringing out, is placed in the wheel. There is then drummed into the leather just as much Spruce Extract and in as concentrated a form as the leather will absorb. Instead of drumming in the Spruce, the leather may be placed in a concentrated Spruce layaway and after being thoroughly saturated is put directly into the wheel without wringing. With the wheel revolving there is then run in through the axle-hole enough 15 per cent solution of the syntan to thoroughly saturate the hides. The wheel is revolved for fifteen to twenty minutes.

The addition of the syntan solution at this point will precipitate the Spruce Extract in a solid form directly into the leather and at the same time will have a very decided bleaching effect. This precipitate is very light colored and of a soft silky nature. It is difficultly soluble in water. The leather can be weighed to its limit in this way. This procedure will give a very light even colored piece of leather, will clear the grain and will add weight.

After this treatment it is often not necessary to soda-acid bleach. If however further bleaching by soda-acid is considered necessary a very much weaker bleach can be used.

In the oil wheel the addition of the syntan to the usual dope or ingredients will give the leather a lighter and more regular color. The procedure is to add the syntan to the hot oils or dope. After thoroughly mixing by stirring, the usual method of adding the oils or dope to the leather is followed.

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NOTES ON WATER EXTRACTION OF LEATHER*

By F. P. Veitch and R. W. Frey

Discussions and results on the water extraction of leather, like the poor, seem to be ever with us. Several committees and independent operators have worked on the subject and much data have been submitted. As a matter of record and as a further contribution to these data, the following tables have been compiled from the records of the Bureau of Chemistry. As will be seen, they have a direct bearing on recent committee work. Most

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of the work was done some 8 or 10 years ago and that presented here should be credited to Messrs. R. F. Steward, J. S. Rogers and C. F. Speh. These data are also supported by other work done in the Bureau.

The extractions were made with a battery extraction apparatus designed by the Bureau of Chemistry, which it might be well to briefly describe. It consists of a battery of copper Soxhlet tubes so designed that a thimble fitted with a syphon and carrying the charge of leather is immersed in a water bath, which can be maintained at any desired temperature between that of the water supply and of boiling water. The extract syphons off into an Erlenmeyer flask, in which it is kept boiling. The steam thus generated is refluxed through an outside tube into a condenser above the thimble, from which the condensed cool water drips on to the leather, thus completing the cycle. To prevent undue boiling of the extract, the extraction is made with five changes of water, each about 200 cc. The first portion of the extract is removed at the end of 1 hr.; the second after 2 hrs.; the third after 3 hrs.; the fourth after 4 hrs.; and the fifth after 4 hrs.; making in all an extraction of 14 hrs. with a total volume of 1 liter. The charge of leather is 15 gms. This method was followed in general, and any exceptions to it are noted.

It should be pointed out that the soluble solids figures, whenever given, are actually such, being obtained by filteration as for tannin analysis, and are not simply an aliquot of the extract. Nitrogen figures are the average of closely agreeing determinations made on an aliquot of the unfiltered extract.

Table I gives the figures from extraction at 45°—65° C. for a total period of 47 hrs. Entire duplication of the extractions were made to determine the concordance of the work. In Table II are the results from extraction at 60°—65° C. for a total of 42 hrs. It will be observed that nitrogen was determined in the first and third extracts and that in the latter it is practically negligible, in no case exceeding 0.06 per cent for 7 hrs. extraction. However, with some of the leathers, it seems that their extracts respond to a test for soluble hide with tannin solution, that is, a precipitate was obtained upon adding a solution of tannin to the extract.

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Table III is particularly interesting, in that it shows the results for a total time of 148 hrs. extraction at 30° C. The notes for these figures state that up to and including the next to the last period of extraction all of the extracts showed a very slight but positive precipitate with gelatine-salt and all darkened with iron alum solution. In the last extraction all gave a slight darkening with iron alum but no response for soluble hide.

Table IV contains the data for extraction at 50° C. of some of the leathers included in Table III. The total time being 70 hrs. A notation for these results states that none of the extracts gave a response for soluble hide but all gave a coloration with iron alum. Here again nitrogen was determined in the extracts and was shown to be present in only insignificant quantities.

Consideration of all the extraction figures given shows that in no case was an absolute end point reached. After 40 hrs. extraction at 45°—65° C. from 0.60 per cent to 0.78 per cent was taken out in the next 7 hrs.; after 35½ hrs. at 60°—65° C. from 0.26 per cent to 0.71 per cent was extracted in the next 6½ hrs.; after 120 hrs. at 30° C. from 0.65 per cent to 1.15 per cent as soluble solids was removed in the next 28 hrs.; and after 56 hrs. at 50° C. from 0.79 per cent to 1.13 per cent was extracted in the next 14 hrs. While these figures are by no means negligible, especially when the result at the end of the first period of extraction is compared in each case with the total extracted, it is felt that they were obtained by rather drastic means. It is estimated that the extractions were at the rate of roughly one liter of water every 2 hrs. through the leather. For Table I the extractions during the last three periods settle down pretty well to an average of 0.20 per cent for 2 hrs., which on the estimate of 1 liter of water every 2 hrs. and on the charge of 20 gms. is equivalent to a solubility of 0.040 gms. per liter; for Table II these figures are 0.154 per cent and 0.031 gms. per liter; for the last five periods of Table III they become 0.112 per cent and 0.017 gms. per liter; and for Table IV 0.122 per cent and 0.018 gms. per liter. While these values have been arrived at by approximation, they indicate, with the exception of the first value, a solubility about like that of calcium oxalate in boiling water, or like that of calcium carbonate in CO_2 free water, and somewhat less than that of barium carbonate in CO_2 free water at 24° C.

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Stating the matter another way, from 8 to 20 milligrams per hour were dissolved from the leathers.

As just pointed out the quantity of material extracted after the second and third periods is practically constant. The nitrogen figures for these periods, while not permitting definite conclusions, indicate that decomposition of the hide or leather substance did not occur. This tendency to settle down to a low and more or less constant solubility is also characteristic of the extraction of tanning materials. The continued solution of constituents from leather also from tanning materials would seen to be due to either or to both the presence of constituents of low solubility which dissolve as a whole without decomposition, or the hydrolysis of constituents which yield to solution certain decomposition or hydrolysis products but not to decomposition of hide substance or collagen. The evidence so far available, however, does not justify a positive conclusion as to just what is taking place.

In Table V a direct comparison is made as far as possible of the data from Tables III and IV to show the extraction of the same leathers at 30° C and 50° C. respectively. For 42 hrs., at least, the extraction at 50° C. gives the higher results for soluble solids although in two cases the difference can hardly be considered significant. It may be pointed out that the sum of the non-tannins for the first two 14 hrs. periods at 30° C. check those for 50° C. remarkably well, with the exception of sample No. 2126, in which results there is evidently an error. The soluble solids for the first 14 hrs. extraction at 50° C. are in all cases appreciably higher than at 30° C. but for the next two periods it will be noticed that the extractions at 30° C. are somewhat higher than those at 50° C., which would suggest than at least part of the extract is from solubility as influenced by temperature and not from decomposition as a result of increased temperature. However, figuring by proportion, the extraction for 70 hrs. at 30° C. from Table III and comparing with the same leathers for 70 hrs. at 50° C. as shown in Table VI, it will be observed that in three out of five instances the extraction at 50° C. for 70 hrs. gives appreciably higher results and that the differences are of about the same order as in Table V. This would indicate that if the

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TABLE I. Water Extraction of Leather by Bureau of Chemistry, Old Method.

Continuous extractions—Hours.			20	+7	+6	+7	+7	Total 47 hrs.
Temperature of extraction—°C.			45-55	45-55	45-55	45-65	55-65	
Volume of extract—cc.			1000	300	300	300	300	
L. & P. No.	Description	%	%	%	%	%	%	%
1394	Texas oak	Total solubles	23.82	1.01	0.72	0.67	0.78	27.00
		Non tannins	6.79	0.32	0.22	0.20	0.25	7.78
"	" "	Total solubles	23.88	0.84	0.65	0.74	0.78	26.89
		Non tannins	6.85	0.21	0.13	0.13	0.19	7.51
1395	Texas oak	Total solubles	32.52	0.83	0.57	0.65	0.70	35.27
		Non tannins	18.15	0.22	0.18	0.24	0.27	19.06
"	" "	Total solubles	32.37	0.63	0.55	0.79	0.72	35.06
		Non tannins	18 23	0.18	0.15	0.25	0.30	19.11
&1396	Hemlock	Total solubles	26.50	0.62	0.59	0.70	0.67	29.08
		Non tannins	11.91	0.16	0.13	0.12	0.15	12.47
"	"	Total solubles	26.79	0.76	0.54	0.57	0.78	29 44
		Non tannins	11.92	0.16	0.06	0.12	0.13	12.39
1397	Oak	Total solubles	21.33	0.92	0.47	0.64	0.70	24.06
		Non tannins	6.45	0.24	0 09	0.23	0.24	7.25
"	"	Total solubles	21.59	0.88	0.56	0.74	0 60	24.37
		Non tannins	6.36	0.18	0.17	0.29	0.19	7.19
1398	English oak	Total solubles	——	0.88	0.57	0.69	0.73	---
		Non tannins	11 59	0 15	0.33	0 19	0.23	12.44
"	" "	Total solubles	30.46	0.85	0.56	0.62	0.60	33.09
		Non tannins	11.56	0 18	0 02	0.19	0.09	12.11
Gms. of dry powder for non tans.			11.75	3.6	3.6	6.1	6.1	

NOTE:—Water changed four times during first extraction; only one portion for each of remaining extractions; 20 gms. of leather for each charge. (0.096) (0.102) (0.103)

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TABLE II. Water Extraction of Leather by Bureau of Chemistry, Old Method.

Continuous extraction – Hours			14.5	7	7	7	6.5	Total 42 hrs.
Temperature of extraction –° C.			60-65	60-65	60-65	60-65	60-65	
Volume of extract – cc.			1000	300	300	300	300	
L. & P. No.	Description		%	%	%	%	%	%
1401	Union	Total solubles	27.98	0.63	0.53	0.68	0.48	30.30
		Non tannins	14.78	0.20	0.18	0.17	0.16	15.49
		Nitrogen in ext.	0.42		0.02			
		React. to gel-salt	+	+	+	+	+	
		React. to tannin	-	-	-	-	-	
1402	Texas oak	Total solubles	26.34	1.32	0.75	0.63	0.57	29.61
		Non tannins	13.35	0.24	0.14		0.24	—
		Nitrogen in ext.	0.07		0.02			
		React. to gel-salt	+	+	+	+	-	
		React. to tannin	-	-	-	-	-	
1403	Hemlock	Total solubles	26.71	1.11	0.57	0 42	0.35	29.16
		Non Tannins	19.19	0.58	0.38	0.20	0.16	20.51
		Nitrogen in ext.	0.07		0.05			
		React to gel-salt	+	+	-	-	-	
		React. to tannin	+	+	+	+	+	
1404	Scoured oak	Total solubles	19.87	0.82	0.53	0.44	0.41	22.07
		Non tannins	7.86	0.28	0.23	0.17	0.17	8.71
		Nitrogen in ext.	0.07		0.03			
		React. to gel-salt	+	+	-	+	+	
		React. to tannin	+	+	+	?	+	
1406	Drum tanned	Total solubles	13.38	1.56	0.92	0.78	0.71	17.35
		Non tannins	3.19	0.33	0.30	0.20	0.16	4.18
		Nitrogen in ext.	0.08		0.04			
		React. to gel-salt	+	+	-	+	+	
		React to tannin	-	+	+	+	+	

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TABLE II. Water Extraction of Leather by Bureau of Chemistry, Old Method. (Continued)

Continuous extraction - Hours			14.5	7	7	7	6.5	Total 42 hrs.
Temperature of extraction -° C.			60-65	60-65	60-65	60-65	60-65	
Volume of extract - cc.			1000	300	300	300	300	
L. & P No.	Description		%	%	%	%	%	%
8352	*Belting	Total solubles	17.23	1.13	0.61	0.57	0.48	20.02
		Non tannins	3.54	0.41	0.16	0.15	0.12	4.38
		Nitrogen in ext.	0.04		0.01			
		React. to gel-salt	+	+	+	+	+	
		React. to tannin	-	-	-	-	-	
8490	*Belting	Total solubles	13.66	0.64	0.54	0.32	0.31	15.47
		Non tannins	4.30	0.18	0.16	0.13	0.09	4.86
		Nitrogen in ext.	0.11		0.02			
		React. to gel-salt	+	+	+	-	?	
		React. to tannin	+	-	+	-	?	
8491	*Belting	Total solubles	16.19	0.62	0.54	0.33	0.26	17.94
		Non tannins	4.57	0.39	0.23	0.15	0.11	5.45
		Nitrogen in ext.	0 14		0.06			
		React. to gel-salt	+	+	-	-	-	
		React. to tannin	+	+	+	+	+	
Gms. of dry hide-powder for non tans.			11.75	4.7	3.5	3.5	3.5	

Note:-

Water changed 3 times during first extraction; only one portion for each of remaining extractions; 20 gms. of leather used for each charge.

*These samples were degreased before extraction.

"React. to gel.-salt"—shows response of extract to gelatine-salt test. A + sign signifying a ppt.

"React. to tannin"—shows response of extract to a solution of tannin. A + sign signifying a ppt.

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TABLE III. Water Extraction of Leather by Bureau of Chemistry, Old Method.

Continuous extraction at 30° C. – Hrs.			14	+ 14	+ 14	+ 21	+ 21	+ 16	+ 20	+ 28	Total 148 hrs.	Remarks.
Volume of extract – cc.			1000	1000	1000	1000	1000	500	1000	1000		
L. & P. No.	Description	%	%	%	%	%	%	%	%	%	%	
2126	Scoured oak	Soluble solids	26.26	2.95	2.66	1.12	1.21	1.72	0.78	1.15	37.85	The extract from next to last one with all leathers showed very slight but positive precipitate with gelatine-salt, and all darkened with iron alum solution. The last extract from all leathers gave slight darkening with iron alum and did not give any response for soluble hide.
		Non tannins	10 44?	0.80	—	0.37	—	—	0.32	—	—	
2127	Scoured oak	Soluble solids	23.03	2 76	1.90	1.60	1.43	1.33	0.94	0.77	33.76	
		Non tannins	12 78	0.44	—	0.33	—	—	0.31	—	—	
2132	Hemlock	Soluble solids	25.18	2 28	1.23	1.03	0.90	0.73	0.62	0.66	32.63	
		Non tannins	16.63	0.51	—	0.28	—	—	0.35	—	—	
2136	Hemlock	Soluble solids	24.32	2.64	1.63	1.33	1.20	1.07	0.80	0.65	33.64	
		Non tannins	14.57	0.49	—	0.28	—	—	0.34	—	—	
9701	Hemlock	Soluble solids	19.20	2.14	1.40	0.83	1.00	1.30	0.77	0.74	27.38	
		Non tannins	10.79	0.42	—	0.30	—	—	0.45	—	—	
9706	Hemlock	Soluble solids	16.07	3.13	2.10	2.30	1.63	1.65	0.93	1.09	28.90	
		Non tannins	6.93	0.56	—	0.42	—	—	0.36	—	—	
9707	Oak	Soluble solids	21.21	2.70	1.92	1.41	1.16	1.10	0.93	0.87	31.30	
		Non tannins	11.26	0.42	—	0.28	—	—	0.37	—	—	
9710	Hemlock	Soluble solids	29.80	2.54	1.76	1 30	1.24	1.20	0.76	0.71	39.33	
		Non tannins	18.10	0.38	—	0.32	—	—	0.36	—	—	
10038	Oak	Soluble solids	13.48	2.93	2.00	1.63	1.63	1.43	0.90	0.80	24.80	
		Non tannins	4.48	0.76	—	0.17	—	—	0.33	—	—	
10364	Oak	Soluble solids	13.93	2.61	2.11	1.42	1.23	1.60	1.01	0.93	24.84	
		Non tannins	3.29	0.40	—	0.32	—	—	0.39	—	—	
Gms. of dry hide powder for non tans.			11.25	10.5	—	5.6	—	—	5.6	—		

Note:—15 gms. of leather for each charge. Leather soaked overnight in H_2O and five changes of H_2O made during each extraction except the 16 hr. one.

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TABLE IV. Water Extraction of Leather by Bureau of Chemistry, Old Method.

Continuous extraction at 50° C. – Hrs.			14	+ 14	+ 14	+ 14	+ 14	Total 70 hrs.	Remarks.
Volume of extract			1000	1000	1000	1000	1000		
L. & P. No	Description	%	%	%	%	%	%	%	None of the extracts gave any response for soluble hide but all gave a coloration with iron alum.
2126	Scoured oak	Total solubles	29.77	2.76	0.97	0.91	0.95	35.36	
		Soluble solids	28.64	2.51	0.93	0.69	0.76	33.53	
		Non tannins	16.29?	0.50	0.42	0.32	0.36	17.89	
		Nitrogen in ext.	0.05	0.00	0.01	0.00	—	—	
2127	Scoured oak	Total solubles	28.60	2.38	1.09	1.22	0.71	34.00	
		Soluble solids	26.66	2.13	1.01	1.12	0.70	31.62	
		Non tannins	12.56	0.51	0.23	0.34	0.17	14.01	
		Nitrogen in ext	0.04	0.01	0.00	0.04	—	—	
2132	Hemlock	Total solubles	28.07	1.85	0.78	0.73	0.84	32 27	
		Soluble solids	26.56	1.52	0.65	0 61	0.74	30.08	
		Non tannins	17.08	0.57	0.36	0.37	0.41	18.79	
		Nitrogen in ext.	0.07	0.02	0.01	0.01	—	—	
2136	Hemlock	Total solubles	28.46	1 95	1.09	0.59	1.13	33.22	
		Soluble solids	27.63	1.91	1.07	0.57	1.07	32.25	
		Non tannins	14.45	0.56	0. 7	0.32	0.44	16.14	
		Nitrogen in ext.	0.06	0 00	0.01	0.01	—	—	
9710	Hemlock	Total solubles	36.39	2.17	0.96	0.90	0.79	41.22	
		Soluble solids	33.86	1.98	0.90	0.93	0.71	38.38	
		Non tannins	17 96	0.46	0.29	0.34	0.33	19.38	
		Nitrogen in ext.	0.04	0.01	0.01	0.01	—	—	
Gms. of dry hide powder for non tans.			8.5	7.0	6.5	2.2	2.1		

Note: 15 gms. of leather for each charge. Leather soaked overnight in H_2O and five changes of H_2O made during each extraction.

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TABLE V. Comparison of Extraction at 30° C. and at 50° C., Assembled from Tables III and IV.

Continuous Extraction—Hrs.				14	+14	+14	Total 42 hrs.
L. & P. No.	Description	%		%	%	%	%
2126	Scoured oak	Soluble solids	@ 30° C.	26.26	2.95	2.66	31.87
			@ 50° C.	28.64	2.51	0.93	32.08
		Non tannins	@ 30° C.	10.44?	0.80	—	—
			@ 50° C.	16.29?	0.50	0.42	—
2127	Scoured oak	Soluble solids	@ 30° C.	23.03	2.76	1.90	27.69
			@ 50° C.	26.66	2.13	1.01	29.80
		Non tannins	@ 30° C.	12.78	0.44	—	—
			@ 50° C.	12.56	0.51	0.23	—
2132	Hemlock	Soluble solids	@ 30° C.	25.18	2.28	1.23	28.69
			@ 50° C.	26.56	1.52	0.65	28.73
		Non tannins	@ 30° C.	16.63	0.51	—	—
			@ 50° C.	17.08	0.57	0.36	—
2136	Hemlock	Soluble solids	@ 30° C.	24.32	2.64	1.63	28.59
			@ 50° C.	27.63	1.91	1.07	30.61
		Non tannins	@ 30° C.	14.57	0.49	—	—
			@ 50° C.	14.45	0.56	0.37	—
9710	Hemlock	Soluble solids	@ 30° C.	29.80	2.54	1.76	34.10
			@ 50° C.	33.86	1.98	0.90	36.74
		Non tannins	@ 30° C.	18.10	0.38	—	—
			@ 50° C.	17.96	0.46	0.29	—

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TABLE VI.

Comparison of Extraction at 30° C. and at 50° C. for 70 Hrs.

Calculated for 30° C. from Table III.

L. & P. No.	2126	2127	2132	2136	9710
Sol. solids at 30° C.	33.39	29.77	30.02	30.32	35.81
Sol. solids at 50° C.	33.53	31.62	30.08	32.25	38.38

extractions are approaching a limit, the limit apparently is different for each temperature.

In Table VII are given some results recently obtained by Mr. I. D. Clarke. The first two extractions were made in a Reed-Churchill extractor by the A. L. C. A. official method; the last three sets of figures were obtained as stated in the table, by soaking the leather residue in two liters of water for the time given. Here again it will be noted that there is no definite end point, but instead a continued low solubility thus confirming the previous results.

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TABLE VII.
WATER EXTRACTION OF LEATHER.

L. & P. No.	Description of leather	Soluble solids 50° C.				Leather residue from soluble solids soaked over night with 2 l. water. Soluble matter					
		1st 3-hour period		2nd 3-hour period		1st. soaking 18 hrs 24.5° C.		2nd. soaking 18 hrs. 27° C.		3rd. soaking 42 hrs. 24.5° C.	
		gms. per 100 cc.	%	gms. per 100 cc.	%	gms. per 100 cc.	%	gms. per 100 cc.	%	gms. per 100 cc.	%
38782	Oak	0.3925	26.16	0.0435	2.90	0.0085	(1) (4) 0.56	0.0035	(1) (4) 0.24	0.0033	(1) (5) 0.22
35265	Oak	0.4080	27.20	0.0409	2.72	0.0088	(2) (4) 0.58	0.0046	(2) ( ) 0.30	0.0044	(1) (5) 0 30
34588	Hemlock	0.3716	24.78	0.0319	2.12	0.0082	(1) (6) 0.54	0 0041	(1) (6) 0.28	0.0043	(1) (6) 0.28
35446	Hemlock	0.4463	29.76	0.0375	2.50	0.0079	(1) (6) 0.52	0.0038	(2) (6) 0.26	0 0043	(1) (6) 0.28
34523	Union	0.3606	24.04	0.0372	2.48	0.0091	(1) (3) 0.60	0.0038	(1) (4) 0.26	0.0047	(1) (5) 0.32
34543	Union	0.3861	25.74	0 0370	2.46	0.0088	(1) (4) 0.58	0.0038	(1) (6) 0.26	0.0048	(1) (5) 0.32

(1) No ppt. with gelatine salt, nor with tannic acid.
(2) Very slight ppt. with gelatine salt,—none with tannic acid.
(3) Slight coloration with iron alum.
(4) Very slight " " " "
(5) Trace of " " " "
(6) No " " " "

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Discussion

After the reading of the Committee report on the extraction of water solubles from leather, the paper by F. P. Veitch and R. W. Frey which is given above was read. Upon its conclusion the following discussion took place.

President Small: The work of this Committee seems to have been mainly unsettling. Our present official method of determining water solubles gives results which are fairly concordant but on the other hand, the criticism is perfectly just that it determines an indefinite quantity. We determine a certain amount of material that is removed from the leather, but whether it is material that was not combined with the leather originally or whether it is material that was partly combined and partly uncombined, or just what, we do not know, and the work of this Committee seems to have left us still in the dark.

The fact demonstrated in the Committee work, that you can extract leather with water more or less indefinitely and still remove material is not especially new. If I am not mistaken, Mr. Veitch has brought it to our attention a good many times. Nearly all of you have to make more or less water solubles determinations every week. There should be a sufficiently active interest to produce a full discussion of this subject.

Dr. Balderston: I believe that when you do the official extraction at 50 degrees, the residue is not leather. I don't know what the definition of ground-up leather ought to be, but careful examination of very many samples makes me think that extraction at 50° is too drastic, since the residue is, it seems to me, not leather. It is decomposed to such an extent that it sticks together and makes a mass that it would take a very long stretch of the imagination to call leather. I think that is a reason (perhaps not a conclusive reason) for believing that 50° extraction is too drastic.

Mr. Frey: In that connection I cannot quite agree with Dr. Balderston because we use what is left after the extraction, of course, for the insoluble ash, and just lately we have been working on quite a number of samples and I know, in breaking them up to help the drying, the residues still look very much like leather. I haven't noticed any evidence of their losing very much of the appearance of leather.

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DR. BALDERSTON: The difference between Mr. Frey's observations and mine is perhaps because of the difference in the character of the leather extracted. Perhaps it would be safer to say that in the case of many kinds of leather the residue does not seem like leather.

MR. VEITCH: Mr. President, it would be an interesting thing, it seems to me, if some one would make a more detailed study of the residue, that is, the form of the nitrogen in it. If we could prove conclusively that the form in which the nitrogen is combined in that extractive material has undergone considerable change, I think we would be justified in drawing the conclusion that some decomposition had taken place. If, on the other hand, it was shown by careful work that the form of nitrogen after extraction was practically identical with that before, I think we would have to acknowledge that there was practically no decomposition of the leather substance itself.

It seems to me also that it might very well be that we might have leather, let us say actually leather that had combined in it possibly 40 per cent of tannin, and still have leather when we had 35 to 30 per cent of tannin. I don't know—that needs further investigation and study. Just along that line, the form of the nitrogen in there should be ascertained. I think it is up to somebody to do some work on it and try to throw some light from that standpoint on this subject.

MR. STACY: We read with interest the work of the Committee and the results that they obtained throughout were interesting. We were happy to know that some of the collaborators found a place where there was a definite end point to the extraction. That question has bothered us for sometime and we once set out on that tedious journey to find out if there was any place where there would be a definite end point to the extraction, but after we got to the sixteenth or eighteenth liter we gave it up as a bad job, thinking perhaps that our Association would never call on us to run any method that would ask for eighteen or twenty liters. We noticed that in the last liter we took off, we still had a coloring matter something similar to what it was in the eighth or tenth liter. We noticed also in the Committee's report some conflicting statements by the different collaborators, and, according to the old axiom, when there are two conflicting

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statements one must be false, we set about to see if we could determine which one of them was correct.

The statement that I have reference to is that the higher the temperature of extraction, the less matter is extracted. So we prepared a sample of leather and ran a series of extractions, to determine, if we could, the critical temperature. What I mean by the critical temperature is that temperature which, if you exceed, you will get less matter extracted than you would if you had extracted your leather at a lower temperature. So we chose the temperatures of 30, 50, 60, 65, 68, 70 and 75° C., and while there was nothing definite found out, yet we thought it might be interesting to give the results of that extraction.

First we corroborate the assertion that the higher the temperature within certain limits, the more matter is extracted. I think you will recall that the Committee of which Mr. Terrasse was Chairman last year found it out very definitely up to within certain limits. We found in this particular sample of leather, which was nothing but a vegetable tanned sole leather, that extracting at 30 degrees we got approximately 25 per cent of water soluble; at 50 we get 30 per cent; at 60° we get 32.26 per cent; at 65° we get 32.12 per cent; at 68° we get 31.70 per cent; at 70° we get 31.96 per cent and at a 75° we get 34.58 per cent. You will notice that there is a gradual rise in the percentage of matter extracted by water up to 60 degrees anyway. Then there is a gradual decrease from 60 to 68 degrees. But when we get up to 75 we have a big jump back. If we notice the character of these solutions after they are cooled, we will notice that at a temperature of 68° we get a slight turbidity. Up to this time the solution has been brilliantly clear unfiltered; and when we get to the 75° extraction we find that the solution is muddy light brown, changed in its character altogether. It is also noted that the insoluble matter in the 75° extraction is 2.64 per cent, showing that there is a decomposition substance at such temperatures.

Then we took these solutions and attempted to analyze them by the official A. L. C. A. method of tannin analysis and we notice that the non-tans of the 30° extraction are 12.42 per cent and at 75° 14 per cent. There is a gradual rise from 12.42 to 14 per cent. However, the tannin figure was a little surprising in so far as at 30° we got 12.55 per cent tannin; at 60° we get

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our highest figure for tannin, that is, 18.82 per cent. This is the analysis of the extract after it has cooled down; the leather has been extracted by the official A. L. C. A. method, and the extraction at 75° gave us 17.94 per cent of tannin.

It was a little surprising to read the remark that the higher the temperature the less matter extracted. We could not conceive of it, so we went to the trouble of trying to duplicate the method as outlined by the Committee and we took a 250 cc. bottle and inserted eight grams of leather, closed it with a rubber stopper with a thermometer in it. We put water in at 50° and rotated it for one hour, and every five minutes we noted the temperature, to see just what was going on, what temperature they had when they were rotating this for one, two or three hours at a 50° temperature, and it was interesting to note that the highest temperature we could read was 47.2° C. The first five minutes the temperature dropped to 40.2°; the next five minutes it dropped to 37.2°, and then in the next fifteen minutes it dropped to 31.2°. It remained around 31 and 30 for the next fifteen minutes, and the last fifteen minutes of extraction it was actually below 30 degrees. So we see during the last fifteen minutes the temperature at which the leather was extracted was actually below 30 degrees, though they say that the extraction was at 50°, and for half an hour the extraction was just either above or below 30°, and for the first fifteen minutes it dropped from 47.2 down to 35.2. So I really think that the Committee's work on the 50 degree extraction by the shake method was more around 30 degrees; we have evidence of the fact that it was below 30°, and I think that explains the reason why they got probably a lower percentage of extractive matter with their 50° extraction than they did with the 30.

This work we have done only corroborates the work that the Committee last year and other collaborators have done, that with every 5 degrees rise in temperature there is approximately nine tenths of one per cent increase in water soluble.

MR. ALSOP: Why use hot water in extracting the leather, why not use cold water?

PRESIDENT SMALL: That is a very pertinent question.

What ought we to try and determine as water-solubles?

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MR. ORTHMANN: I have really never seen the reason why we should use hot water, because sole leather as a rule is never subjected to those conditions; when it is on the shoe it always meets with cold water, at practically room temperature, no higher than 80° F. in summertime or 90° F. at the most.

MR. VEITCH: I don't think we need any explanation as to why we use hot water.

MR. ORTHMANN: There is no reason for it.

MR. VEITCH: There is a good reason for it. We do it on the assuption that the soluble material is a little more soluble in hot water than it is in cold, and we are supposed to be dealing with another material that is not soluble. You might say there is a good deal of assumption in there, but that of course is the basic assumption upon which we have been doing it, that the matter that is actually soluble is more soluble in hot than in cold water, like most things, (it is not always true but it usually is true) and we get results quicker; it hastens the work. Of course, if hot water actually attacks the combined leather and removes something during the period of extraction, it ought to be abandoned. That is the point that ought to be investigated, it seems to me.

DR. BALDERSTON: There is only one bunch of people that I ever heard of, who made soup out of their boots, and they were in Captain Cook's boat on the Pacific. What we are driving at in this extraction is not to see how much soup we can make out of our boots.

MR. ALSOP: Mr. President, if hot water does not remove the tannin that should not be removed, why is it that the solutions from later extractions contain more tannins in proportion to the non-tannins than the first?

MR. VEITCH: Mr. President, it seems to me that there is an assumption in Mr. Alsop's question that is not entirely justified. He asks a question and makes a statement at the same time.

MR. ALSOP: You just said so in your paper.

MR. VEITCH: That there is more tannin? No, I didn't say that. If I did, I want to withdraw it. I think it is sometimes the case, but I don't think it is usually true, and I think that easily could have been accounted for by the fact, that we all know, our method is not accurate to small fractions of a per cent.

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PRESIDENT SMALL: Mr. Hayes in my laboratory took a piece of the centre or butt portion and a piece of the flank portion of a tanned hide and extracted the two under the same conditions. The amount extracted was radically different in the two cases but, (stopping at a point where the amount of material extracted by each additional liter was a constant and small amount) the percentage composition of the final leather residues attained, was identical, or practically so, in the two cases. Further tests may or may not confirm this but if they did one could draw the very pleasing inference, that there is a specific combination of collagen and tannin which is arrived at when extraction under given conditions is carried to an approximate limit.

MR. ALSOP: This work throws some light on the value of the figures for combined tannins. Generally in the report of the analysis of leather by different methods of extraction the water solubles may vary 10 per cent to 15 per cent.

MR. VEITCH: I find in looking over our figures here, there are a few of them of the character that Mr. Alsop speaks of, that is, where the tannin is as high, or in some instances a little bit higher at the last extraction, than it was several extractions ahead, forty hours ahead perhaps, but as a rule our figures in nearly every case would tend to show decreased tannin rather than increased tannin.

There is another influence in here; I don't know how great it is, but it must be borne in mind in discussions of this kind. Where total solids or solubles are made under one set of humidity conditions and the non-tannins are made under another humidity condition there will be small errors. In other words, there are operating errors in all of this work, that we must not scan the figures too closely on one tenth or two tenths difference; even if it is higher in the later stage of extraction, it must not be given too much weight, it seems to me. For instance, here is an instance where the soluble solids ran like this: In the first 14 hours 27.63; in the second 14 hours 1.91; in the third 14 hours the soluble solids were 1.07; in the fourth 14 hours 0.57, and in the fifth 14 hours it went back to 1.07 per cent. I don't know just why, but results like that are often obtained.

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PRESIDENT SMALL: Has any one any suggestion or any line of attack to offer that might be brought to the consideration of a committee that may be appointed to study this another year?

MR. OBERFELL: Is it possible to determine nitrogen in the extract, and thus arrive at a point at which decomposition might take place?

MR. VEITCH: We never have been able to find any quantity of nitrogen in solution in the water extract, though we have run hundreds of tests. Even after extracting with 60 or 70 liters of water continuously no nitrogen was found in the final extracts.

MR. STACY: May I ask Mr. Veitch what was the highest temperature at which he did not find any nitrogen?

MR. VEITCH: We never worked over 60 or 65° C. It is so obvious that around boiling point of water, at even above 65°, there is going to be decomposition, that it did not seem worth while to go further.

MR. STACY: That was the very point I wanted to bring out, Mr. Chairman, that our extraction at 75° gave us a very muddy solution and that there was a certain decomposition substance in it, and we assumed (though we never determined the nitrogen) that there was nitrogen in the extraction from 70° to 75° anyway.

MR. SCHULTZ: I am inclined to doubt Mr. Stacy's assumption that there was nitrogen present in such an extract because in the Committee work, when adding water at 95° to an eight gram sample and shaking it, although the character of the sample was changed from fibrous to a powder like material only a trace of nitrogen was found in the solution.

MR. VEITCH: I don't think the two experiments were parallel. Mr. Stacy got a muddy solution or extract at a temperature higher than 50° C. and maintained constantly at 75° C. Probably this muddy solution did contain nitrogen. Mr. Schultz started at 95° C., but the temperature dropped immediately, as Mr. Stacy shows, to 30°, thus giving an entirely different set of conditions. One extract might very well contain nitrogen and the other might not. I think even at 60 to 65° C. some nitrogen may ultimately be dissolved.

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PRESIDENT SMALL: Mr. Mlejnik, do you remember whether Mr. Hayes, when he extracted samples of leather in a Soxhlet apparatus, made a determination of the hide substances in the water extraction?

MR. MLEJNIK: He did. The hide substance seemed to go into solution at high temperatures and the extractive solutions on cooling showed turbidity. Mr. Schultz might have had some sort of solution at high temperatures but his shaking mixture cooled, probably throwing it out, whereas Mr. Stacy extracted at a high temperature and as a result the solution was turbid. Possibly the turbidity could have been filtered off in Mr. Stacy's case and the filtrate found practically free from nitrogen. As a result of this, there is a great deal of difference between the two. Mr. Hayes found that on extracting with a Teas extractor the resultant extractive did contain hide substance.

MR. STACY: We found on extractions up to 60°, including 60°, that we got no insoluble; the turbidity of the solution began at 65, and we got .07 per cent insoluble; at 68° we got 1.17 per cent insoluble, at 70° we got 1.58 per cent insoluble, and at 75° we got 2.64 per cent. However, after this solution is filtered through the kaolin paper we go back to the original color, only a little lighter, and we no longer have that light brown muddy solution.

BOOK NOTICE

HAUT-UND LEDERFEHLER (HIDE AND LEATHER DEFECTS). By R. Lauffmann. Vol. IV of the Tanner's Library. 69 pages. Verlag Technischer Zeitschriften G. m. b. H., Teplitz-Schönau, Czechoslovakia. Price $1.00 net.

The author has assembled all of the defects found in finished leather, some sixty in number, which are due to original defects in the hides or skins or to faulty operation in the tanning processes These are treated in alphabetical order. A description of the appearance of each defect is given together with its cause and, where it is possible and known, the means of preventing the defects is given. Each item is treated briefly and concisely while complete literature references are given to articles on the various subjects. The book is to be recommended, if for no other reason, in that it presents, assembled and in compact form, a wealth of knowledge on the subject that has heretofore been widely scattered throughout the literature on tanning.

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ABSTRACTS

Synthetic Tannins. ANON. *Lea. Tr. Rev.* **54**, 374 (1921). The name synthetic tannin is applied in practice to mean those bodies which are made by chemical reactions similar to the one employed by Stiasny in making neradol. There are a large number of such products on the market to-day and caution is advised in selecting them for use. Some causes for unsatisfactory products are:— (1) Use of insufficiently purified materials. Some contain pyridine which gives an objectionable odor to the leather. (2) Inefficient control of temperature of the reaction. This causes the production of resinous bodies in a state of fine suspension and gives a bad coloured, half tanned leather. (3) Insufficient neutralization gives a product with excellent bleaching properties but the leather formed from it is hard and tinny and low in weight. (4) Over neutralization gives a product which penetrates poorly and leather from it is not of good color.

The advantages in the use of synthetic tannins are:—(1) Their power of protecting the grain and fiber when used as a preliminary tanning agent thus making it possible to use stronger liquor than normal. (2) Their power of accelerating the speed of tanning when used with ordinary vegetable tanning materials. (3) Their plumping properties due to the relatively high acidity and (4) their bleaching properties. Distinct disadvantages are found in their low weight giving and exceedingly high cost.

In use, pelt should be appreciably delimed before being placed in solutions of synthetic tannin also in fat liquoring light leathers no alkalies should be used hence emulsions free from soap are used.

In the manufacture of sole or strap leather the total weight of syntans used should not exceed 5 per cent of the pelt weight as extensive use tends to give low weight. Their value lies in speeding penetration, plumping and in giving good colour. They are used to advantage in the first suspenders and in bleaching.

In the manufacture of dressing hides, split hides, vegetable tanned kips and calf skins, synthetic tannins find considerable use. For such goods synthetic tannins may either be used as a preliminary tannage or added to the suspender liquors. They may also be used for retanning East India tanned leather after stripping with borax and washing.

In the manufacture of chrome upper leather a preliminary tannage in a 5° barkometer liquor of syntan is said to give good results while for chrome belting and white chrome leather it is becoming common practice to give a final bleach by drumming with syntan.

Skins which are to be finished in the hair may be tanned by replacing the usual tannage with syntans. After preliminary preparation the skins are drummed in a 2 per cent solution of synthetic tannin which is gradually strengthened to 5 per cent. The same procedure may be substituted with good results in the manufacture of alum tanned sheep skins for smiths' aprons; of horse hides for heavy hedging gloves and for edging the sails of fishing vessels; and for lamb skins for masonic aprons.

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Mangrove. By J. A. Pilgrim. *Lea. Tr. Rev.* **54**, 378 (1921). The term "mangrove" is more or less indescriminately applied to the many varieties of trees which take root in the alluvial deposits at the mouths of great rivers in tropical regions. The species found in the various mangrove swamps of the world resemble each other but the predominating trees are not always the same. For trees of the same species growing in different places it has been found that there is a wide variation in tannin content. The author found that the mangroves of the Pacific Islands appear to increase in richness the further south they were found. The bark of *Rhizophora mucronata* from the Philippines appeared somewhat less rich in tannin than that collected in North Borneo and this in turn less rich than that in the south of Sarawak.

As the mangroves grow in a more or less salty medium it is to be expected extracts from any portion of them contain chlorides. A common mangrove extract will not contain less than 2 to 3 per cent of chlorides. The presence of chlorides in these extracts is not due to salt being encrusted on the bark but it is incorporated in the substance of the tree. Hence the chlorides cannot be removed by washing of the bark without a corresponding loss in tannin. The percentage of tannin in the bark generally seems to increase from tip to base of the tree while chloride content increases from the base to the tip.

Upholstery Leather. Anon. *Lea. World.* **13**, 500 (1921). The class of hides used comprise buffalo and steer hides. The chief characteristic of upholstery leathers is looseness and softness of feel in addition to an extreme pliability. The hides are soaked, limed in a lime containing sulfide, unhaired and fleshed after which they are given a fresh lime without sulfide in which they remain for 4 to 5 days. They are taken from this lime and split. The grain splits are bated, scudded and washed in warm water when they are ready for tanning which may be done either in pits or drums. Such leathers may be finished in a great variety of colors and grains. They are usually made to sample submitted. The author describes a method of finishing in two colors.

Tannin from the Viewpoint of Biological Chemistry. Anonymous. *Halle Aux Cuirs,* May 15, 1921, 129-31, Bohn and Drzewina (*La Chemie et la Vie*) conclude that plants do not throw off toxins or unassimilated products, such as the tannins, because they do not have organs for excretion, but render them harmless through cyclisation. Fletcher (*Memoirs Ag. Dept. India,* Botanical Series V, II) believes that sometimes plants secrete substances toxic to other plants as well as to themselves. Mukerji (*Agri. Jour. India,* Sept., 1920, 502) in attempting to confirm Fletcher's work conducted some experiments with Knop's nutritive solution instead of spring water. He used a large number of plants including particularly wheat, Cajanus, and Bouteloun and found that plants in those solutions in which other plants had previously grown flourished better than in the concentrated solutions in which no plants had pre-

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viously grown and that those in distilled water developed still better. From this he was led to believe that Fletcher's results were due to the concentration of salts in the spring water and not to toxic secretions. The concentration of the solutions used by Fletcher was about 1.12 per cent which is necessarily toxic for any plant. All of these experiments would seem to confirm Bohn's conclusions.

R. W. F.

Deliming by Lactic Fermentation. By Pascal Huc. *Halle aux Cuirs,* May 15, 1921, 141-44. The well known fact that lactic ferment develops well in whey when in contact with albuminoid material and a neutralizing agent led to some experiments using whey, especially as the hides would seem to be a choice source of albuminoid matter and the lime in them would serve for neutralization. Repeated experiments, however, at the ordinary temperature using diluted whey, seeded with lactic ferment, always produced dull gray stains on the grain due to groups of micro-organisms (*bacillus megatherium*). Sometime ago, Eitner showed that such defects had the same origin in the use of bran and excrement bates. The above experiments being conducted in open vats were thus exposed to contamination from the air but repetition of the work in previously scalded closed vats gave the same results. It was then thought that working at higher temperatures, 35° to 38° C., with especially selected lactic ferment would give conditions favorable to its development while the mucor-organisms of the tannery accustomed to a lower temperature would not thrive so well. Deliming in this manner at 35° C. was very successful. The lactic fermentation predominated with rapid deliming, being complete in 3 hours. The bath of whey and water was of such a concentration that there were present 2 kg. of lactose per 100 kg. of white hide. After removing the skins the bath was allowed to cool. Butyric fermentation became evident in a few hours followed soon by a putrid fermentation. It is concluded that deliming can be successfully done by fermentation of whey under the influence of specially selected lactic ferment but that it is necessary to operate at a temperature of 35° to 38° C. to avoid parasitic contamination.

R. W. F.

Unification of Filtration in Tannin Analysis. By E. Schell. *Le Cuir* 10, 143-4 (1921). If tannin analysis is to be developed to a high degree of accuracy the principles of logic, precision and equity must be applied. The first important question is that of filtration. The use of the porous candle would appear to deserve critical examination. Logically it is not necessary and not being applied to the detannized solution is not consistent. Repeated use of the same candle gives quite different filtering properties depending upon the service required of it and upon the nature of the solution filtered. A new candle does not give the same results as a used one, which causes discordant figures by different analysts, or by the same person at different times. As a candle can be cleaned only superficially of the insolubles deposited within its walls there are

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left varying quantities of these materials which influence the determination in many ways and might even be considered sometimes to have a detanning influence. It does not seem safe to rely upon such a filtering medium and in this connection a given filter paper, with a separate piece for each determination, appears to be infinitely superior. Finally there must be considered the effect of the candle upon the color of the solution, in those cases especially where the color readings enter into the commercial valuation of the extract. In support of the filter candle it must be admitted that there are isolated cases, as with certain natural quebracho extracts difficult to filter, in which the candle because of its filtration power, might be preferred. R. W. F.

The Mangroves of the French Colonies. By HENRI JUMELLE. *Le Cuir* 10, 206-9, 1921. As reference for surveys on the tannin materials of the colonies the distribution of the important varieties of mangrove, *Rhizophora*, is given. Considerable analytical data on the tannin content of the bark of various mangroves have been assembled from several sources to show the wide variation in tannin with different localities and varieties and also the effect of age and ross. As illustrating the influence of age the tannin content of a series of well rossed and dry barks of Australian *R. mucronata* is given as follows: 28.2; 30.3; 34.0; 38.6, and 40.4 per cent for tree trunks 10, 20, 25, 30, and 40 cm. in diameter respectively. In a series of 21 samples of the same variety of bark from the Philippines the tannin ranged from 12.3 to 33.8 per cent for trunks from 20 to 45 cm. in diameter. The ross being very poor in tannin greatly reduces the tannin content of the bark. In one case where the sound bark contained 30 per cent tannin the ross gave only 5 per cent; in another sample from Madagascar the ross contained only 2.4 per cent and the bark 12 per cent. With some samples from Mauritius the ross runs from 1 to 4 per cent and is abnormally thick. While the ross with most of the barks averages about 25 per cent of the total bark with these samples it corresponds to 40 to 45 per cent of the bark.

As with other barks the condition of mangrove barks and the curing or drying of them greatly influence the quality. Imperfectly dried barks undergo alteration and the mold which forms, especially the *Sterigmatocystis nigra*, can cause destruction of tannin, while exposure to the air and light cause in addition an oxidation with the simultaneous reduction of the tannin content and increase of coloring matter. The time of gathering may also have an influence. For example the barks of East Africa which are gathered near the end of the year give, probably because at this time the drying is most readily and rapidly done, a comparatively fair leather which furthermore upon exposure becomes a yellowish brown instead of a reddish brown. This is of interest since the same barks of *Rhizophora* and even *Bruguiera* gathered at other times give a strong red color to the leather upon exposure. All of this illustrates the value of observations and experimental work to determine the best condition for yielding the maximum value of the barks. R. W. F.

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Notes on One Bath Chrome Tanning. By E. GRILICHES. *Coll.* 611, 127-9 (1921). [See This Jour. p. 286, (1921).] In reply to the criticism of Stiasny, Griliches states that he used pickled skins to follow commercial practice and to preserve the skins since the experiment required over half a year. Also the effect of this acid on the acid absorbed by the skin was probably overestimated. The results are not absolutely correct since the present methods are poor but the results are comparable in themselves.

I. D. C.

Reply to R. Lauffmann's Article on the Shake Method and the Filter Method. By G. BALDRACCO and S. CAMILLA. *Coll.* 611, 125-7 (1921). The authors review briefly their previous publications [See This Jour. 15, 201, 544 and 545 (1920),] describing a modified shake method for tannin analysis. The per cent tannin found by the filter method is too high since some nontannin is absorbed, while by the official shake method of the I. A. L. T. C. the tannic acid is not all removed from certain extracts.

I. D. C.

The Determination and Retention of Free Sulfuric Acid in Leather and Hide. By C. IMMERHEISER. *Coll.* 611, 132-5 (1921). A reply to the criticism by Moeller of Immerheiser's method (see Coll. 1920, p. 465, This Journal 16, p. 287) "Loss of sulfuric acid through reduction by organic matter is negligible for after evaporating to dryness 20 cc. of 10 per cent tannin solution and 20 cc. of N/10 sulfuric acid, 0.098 gms. of acid was found in the residue while 0.101 gms. had been added. This method is not based on a "neutralization theory" as Moeller states. By analysis most of the acid is found to be combined and since an equivalent amount of base is not found in the leather ash, part of the acid must have combined with organic matter from the hide.

I. D. C.

The Reactions Taking Place During the Oxidation of Unhaired Skins. By W. MOELLER. *Coll.* 612, 161-9 (1921). During the oxidation of the decomposition products of skin the amino-acids are oxidized by hydrogen peroxide with the production of carbon dioxide, ammonia and an acid and an aldehyde each with one carbon atom less per molecule than the original substance. There is a slight tanning action by the formaldehyde but this is soon overbalanced by the hydrolysis of the skin by the acid. Potassium permanganate is a stronger oxidizing agent than peroxide but its action is soon stopped by the deposit which forms on the fibers. Collagen itself is rich in oxygen and is scarecly attacked by permanganate until it has been hydrolysed. Halogens probably do not oxidize collagen but do form insoluble addition or oxidation products with the decomposition products. Chlorine and bromine have no tanning action but iodine and the decomposition products form a brown colloidal solution which is a true tanning system. The amino-acids are oxidized by quinone and chromic acid in the same manner as by peroxide. Too high results will

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be obtained by the iodometric method or by the peroxide method for formaldehyde if the solution contains decomposition products due to previous contact with hide powder or skin.

I. D. C.

Aldehyde Tannage VII. By W. MOELLER. *Coll.* 611, 117-25 (1921). Formaldehyde tannage is similar to all other kinds of tannage except that the action is much more energetic due to the catalytic action of the decomposition products of the hide. A finely pulverized hide powder, which had been prepared without the use of formaldehyde, absorbed 88.64 per cent of formaldehyde in one month from either a 15 per cent or a 30 per cent solution, while 73.64 per cent of neutralized formaldehyde was absorbed from a 15 per cent solution and 77.73 per cent from a 30 per cent solution in the same time. This adsorption is as great or greater than the adsorption of formaldehyde by charcoal. The formaldehyde was not adsorbed as a gaseous film since there was almost no loss on drying the leather at 100° C. for 24 hours. Neither was the formaldehyde taken up in the solid polymerized form for, even after a long time, no polymerization occured in a formaldehyde solution containing pieces of unhaired skin. The formaldehyde had therefore all taken part in the tanning. Pieces of unhaired skins did not absorb over 4 per cent of formaldehyde, but this could be shown under the microscope or by boiling, to be due to the fact that a film of tanned material covered the fibers and prevented penetration.

I. D. C.

An "Insoluble" Hide Powder. By H. R. ZEUTHEN. *Coll.* 612, 181-2 (1921). Freiburg ready chromed hide powder was first washed in the usual way then washed with alcohol until free from water then dried. Comparative analyses with this and with freshly washed powder were made every 1-2 months during the following year, and the results all showed good agreement. The washing and drying with alcohol should precede the grinding or the washing on a large scale will be very difficult. Vienna and American hide powders gave low results probably due to a strong surface chroming which prevented the powder from wetting up properly, but this can be prevented by grinding after chroming and washing. The preparation should be under the direction of a suitable research laboratory.

I. D. C.

The Ability of Hide Powder to Absorb Acid in the Presence of Formaldehyde, with Special Consideration of Acid Dyes. By O. GERNGROSS. *Coll.* 612, 169-81 (1921). Moeller (*Coll.* 1920 p. 109, 152, 209, 267, 319, and 382) states that in all work on the adsorption of acids or bases by hide powder or skin, the influence of hydrolysis has been overlooked and that hydrolysis prevents equilibrium being reached between the acid, water and the hide powder. But since acids hydrolyse skin it is necessary to use dilute acid and to allow it to act for only a short time instead of

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for several months as Moeller does. Hide powder which has been lightly tanned with formaldehyde is scarcely hydrolysed at all for the first hour or two and in this time the adsorption is practically complete. In the experimental work a formaldehyde tanned and an untreated hide powder were used which had water solubilities of 44 and 82.7 resp. The adsorption of acid by the two hide powders was determined, using a water blank in every case for comparison. The formaldehyde treated hide powder absorbed less acetic acid in every case than did the untreated powder. The least difference was 26 per cent with a 0.2 N solution and the greatest 46 per cent with a 0.02 N solution. The adsorption of picric acid also was measured and the solutions were analysed colorimetrically as well as by titration, so that amino-acids from the hydrolysis of the hide or formic acid from the formaldehyde could not affect the results. The results by the two methods agreed well. From 10 per cent to 26 per cent less acid was adsorbed by the treated hide powder as the concentration of the acid decreased from 0.07 N to 0.003 N. The adsorption followed the adsorption law to about 0.015 N and then quickly approached saturation at higher concentrations. In this respect the action of hide powder is different from that of silk, wool or carbon. Hide powder also does not give a typical adsorption curve with phenol while carbon does. If the decrease in adsorption of acid caused by formaldehyde is due, as Moeller suggests, to a coating of formaldehyde on the fibers, the adsorption of basic dyes should also be decreased while as a matter of fact it is increased. Also an acid dye which has been adsorbed by hide powder is partially set free if a solution of formaldehyde is added. When solutions of napthalene black and "Biebricher" scarlet were shaken with portions of a mixture of formaldehyde treated and untreated hide powder a mixture of white and colored particles was obtained. The untreated particles only were dyed.

I. D. C.

Present Day Auxiliary Materials for Patent Leather Manufacture. By G. GRASSER. *Gerber*, **46**, 87 (1920). The important raw materials for the production of patent leather are linseed oil and turpentine. For the chemical determination of the purity of linseed oil, a high saponification— and iodine number and not too small a hexabromide yield, is largely considered. Satisfactory age is indicated by not yielding a foam on heating and remaining clear. The lowest possible acid value is desired. Good drying properties are a prime requisite. The method of testing for this property consists in rubbing the oil with sufficient white lead to give a viscous, varnish like mass, which is still capable of being spread well. A thin coating of this mixture is placed on a glass plate and kept exposed to the air at the usual or higher temperatures for several hours. The quality of the oil can be observed by the hardening of the film. Non-drying oils retard this drying greatly or entirely and therefore this method serves as a simple means of detecting adulteration.

Pure turpentine oil is a nearly colorless liquid with a pleasant, mild

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odor. It is well miscible with benzine and petroleum and is frequently adulterated with them. In the air it is oxidized into a colorless to yellowish, viscous, mass, upon which rests its value as a thinner for lacquers. A completely successful substitute for turpentine was produced in Germany and placed on the market under the name of "Tetralin." It is a uniform substance, a tetrahydroxy-naphthalene, with constant boiling point and always the same properties. It is a water-clear, relatively heavy liquid (sp. gr. 0.975 at 15° C.) which is inflammable at 78° C. but only reaches its boiling point at 205° C. The volatility of this product is greater than turpentine but not so great as benzine. In comparison with benzine the fire risk is not so great and the constant boiling point is a decided advantage in that it prevents bubble formation and similar faults in enamels. Tetralin is an excellent solvent for all natural and artificial resins, waxes, oils, fats, varnish and siccatives. Good miscibility with mineral oils. turpentine and various ethereal substances, such as, ethyl acetate and chlor-ethylene, determines the use of this material for all of those purposes where it was considered necessary to use turpentine, also for the production of all varnishes, shoe creams and polishes, split leather finishes and the like. For purposes in which a somewhat quicker evaporation is required or a lower solubility, "Tetralin Extra" is supplied. It is a completely hydrogenated naphthalene, boiling point 185-195° C. and burning point 60° C.

G. W. S.

Disinfection with Milk of Lime of the Hide of Animals Having the Glanders. By L. Pfeiffer. *Ledertechn. Rund.* **13**, 29 (1921). It was found from culture and animal tests that a milk of lime solution (1:30) killed the glanders bacillus in guinea pig skins within 6 hours, and the same is to be assumed for horse hides as was demonstrated by field experiments. There should be no hesitation to use horse hides from animals afflicted with glanders for the manufacture of leather if they are treated with a freshly prepared milk of lime solution of 1:20 for 24 hours. This strength solution and a period of action of 24 hours produces no change in the texture of the hide.

G. W. S.

Contribution to the Knowledge of Quebracho. By L. Jablonski and H. Einbeck. *Ledertechn. Rund.* **13**, 41 (1921). All investigators on the constitution of quebracho have attempted to free the tannin of impurities, which has not always been attended with success. Attempts to split the molecule and isolate cleavage products from the reaction mixture have been made by different investigators. Arata claims phloroglucin and protocatechuic acid are obtained with the potash fusion and decomposition with strong sulfuric acid; also that dry distillation yields pyrocatechin. Geschwendner states that the oil distilling over appears to be guaiacol. Nierenstein reports that protocatechuic acid, phloroglucine, resorcine and quinone apparently are formed by the decomposition of quebracho tannin. The authors confirm the production of protocatechuic acid from que-

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bracho by the potash fusion and also proved resorcine to be a cleavage product, but claim that the investigation of the cleavage products give no support to the presence of phloroglucin. Perkin, Gunnel and Arata isolated the vegetable dye fisetin from the wood of quebracho colorado (*Quebrachia Lorentzü*) which the authors confirm.

The detection of adulteration of quebracho with mangrove by the acetic ester-or molydenum number is made difficult or impossible when the quebracho is heavily sulfited. The authors followed the thought of splitting up the quebracho by oxidation and thus to identify basic substances. When using nitric acid, besides about 30 per cent of oxalic acid, styphnic acid (trinitroresorcine) was isolated from the reaction mixture in considerable quantities. Thus 60 grams of a guaranteed pure extract yielded 5.67 grams styphnic acid, which corresponded to 2.74 grs. resorcine or 4.56 per cent. In order to explain the source of styphnic acid the quebracho extract was treated with resorcine reagents. The test was made by fusing cautiously 1 part of the quebracho with 2 parts of phthalic anhydride in a test tube over a bunsen flame and adding several granules of fused zinc chloride. This mixture was then cautiously heated further over a smaller flame until a solid mass remained. After cooling it was heated with dilute hydrochloric acid, the solution poured off and the sticky residue boiled with water. If caustic soda is added to the filtered aqueous solution until the zinc hydroxide is redissolved then in the presence of quebracho a solution is obtained having the familiar yellowish green fluorescence of fluorescein. Even treated and strongly sulfited quebracho gives this reaction but it was found that it was not given in mixtures with mangrove when the mixtures contained less than 54.4 per cent quebracho and with oak bark extract 33⅓ per cent was sufficient to prevent the reaction. The authors believe that this phenomenon can only be explained by the assumption that mangrove and oak bark extracts contain groups which react in some way with the resorcine residue. Tests with resorcine alone showed that mixtures of 93 per cent oak bark extract and 7 per cent resorcine and 95 per cent mangrove extract and 5 per cent resorcine are the limits blow which the fluorescein reaction will not be obtained, while 5 per cent resorcine and 95 per cent pyrocatechin gives an intense fluorescence. The authors found that this difficulty could be overcome by dissolving the mixed extract in water and extracting with acetic ester and subjecting the residue after distilling off the acetic ester to the phthalic anhydride fusion. In this way it was possible to detect 5 per cent of quebracho in oak bark and mangrove extract. It was found that mimosa extract also yielded styphnic acid when oxidized with nitric acid and gave the fluorescein reaction with the phthalic anhydride fusion. Styphnic acid yielded by mimosa extract was equivalent to 2 per cent of resorcine against 4½ per cent for quebracho. The existence of free resorcine in quebracho extract could not be confirmed. Fisetin was isolated and identified. Quebracho wood subjected to the phthalic anhydride fusion did not give the fluorescein reaction but after standing several hours with water, the aqueous extract filtered off,

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evaporated, and the residue tested, the fluorescein reaction was obtained. The extracted wood did not give the reaction although when extracted again the aqueous extract would give a residue that gave the reaction. This reaction of quebracho extract is not influenced by the tanning process as a strong fluorescein reaction was obtained by subjecting hide powder, tanned in a solution of quebracho of analytical strength, after drying, to the phthalic anhydride fusion. The non-tannin solution did not give the reaction. Authentic pure quebracho tanned leather gave a strong reaction. To detect quebracho in a mixed tannage the leather should be extracted in a soxhlet with alcohol, the residue from the alcohol extraction dissolved in water and extracted with acetic ester. The residue from the acetic ester is subjected to the phthalic anhydride fusion. The authors found that no leathers that were quaranteed free from quebracho tanning materials gave the fluorescein reaction. Mimosa extract remains the one exception and in the course of further study it will be attempted to find a way to differentiate between these two tanning materials.

G. W. S.

On Synthetic Tanning Materials. By C. IMMERHEISER. *Ledertechn. Rund.*, 13, 49 (1921). A criticism of Moeller's treatise on synthetic tanning materials [see Abstract This Jour. 16, 167 (1921).] The author claims that Moeller's assumption that sulfonation is the basic principal of synthetic tannins is false as it is only the means of rendering insoluble materials soluble to permit their use for tanning. Since *B*-naphthalene sulfonic acid is not a tanning material it is not proper to compare its action with that of a material that has a very decided tanning action. The author claims that good serviceable leather is produced by the appropriate use of synthetic tannins and that the whole question hinges on the appropriate use. Just as this determines the successful use of sodium sulfide for unhairing, or materials for bating and plumping hides, or even vegetable tanning materials for tanning.

G. W. S.

The Bateing Action of the Free Sulfo Group in Synthetic Tanning Materials. By W. MOELLER. *Ledertechn. Rund.* 13, 50 (1921). In the previous work on the action of artificial tanning materials [Abst. This Jour. 16, 167, (1921)] it was found that synthetic tanning materials have a double character. They possess a weak tanning action and an energetic bateing action, the latter being due to free sulfonic acids. The author claims that the bateing action of such materials is a function of the concentration, time and temperature. The bating action of compounds containing free sulfonic acids has been known for more than 30 years. Some literature references and patented processes involving the subject is given. The remainder of the treatise is given over to an attack on synthetic tanning materials. The author claims that the present day artificial tanning materials possess only a very weak colloidal nature because they are composed principally of simple free sulfonic acids. Their

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aqueous solutions can only be termed "semi-colloidal" and hence "semi-tanning materials." Tannin analysis gives a false value for such tanning substances since the free sulfonic acids are absorbed by hide powder. A method for analyzing such materials should differentiate between the tanning substances and the hydrolizing free sulfonic acids. In order to separate the free sulfonic acids from the combined it appears that either ultra-filtration or dialysis will have to be resorted to. An investigation of a product sold under the name of "Ewol-Tannin" is reported. This investigation was carried out in the same manner as reported in the previous paper for neradol and ordoval. Into 100 cc. of solutions of 1, 5 and 10 per cent 4.4 grams of hide powder was placed and allowed to stand for 8 days and 1 month. Nitrogen was determined on an aliquot of the solution after filtering off the hide powder and this was calculated to hide substance. The amount of soluble hide found in this way increased with increasing concentration and with increase in time of contact. For a period of action of 8 days the 1, 5 and 10 per cent solutions gave 1.20, 4.17 and 6.79 per cent hide respectively. For 1 month they gave 2.06, 5.51 and 11.27 per cent hide.

G. W. S.

PATENTS

Tanning. Brit. Pat. 157,851. CHEMISCHE FABRIKEN WORMS AKT.-GES., Frankfurt-on-Main, Germany. Jan. 10, 1921. Hides are tanned with the alkaline-earth salts of synthetic tanning-agents of the kinds described in Specification 156,254. According to an example, a mixture of naphthalene and phenol is sulphonated and condensed with formaldehyde solution, the product is diluted, neutralized with lime, and filtered, and the solution used for tanning. The products may be employed alone or mixed with other tanning-agents.

Synthetic Tanning Agents. Brit. Pat. 157,852. CHEMISCHE FABRIKEN WORMS AKT.-GES., Frankfurt-on-Main, Germany. Jan. 10, 1921. *Sulphonic acids.*—Synthetic tanning-agents are prepared from tars or tar oils by coupling the components thereof by appropriate elements or radicals without isolation of the components from the tars or oils, and solubilizing the products by introducing acid groups before or after the coupling.

Synthetic Tanning Agents. Brit. Pat. 157,855. CHEMISCHE FABRIKEN & ASPHALTWERKE AKT.-GES., Griesheim-on-Main, Germany. Jan. 10, 1921. *Sulphonic acids.*—Synthetic tanning-agents are prepared from tars or tar oils by introducing acid groups without isolating the components from the tars or oils, converting the acids into their metal salts, and then coupling these salts by appropriate elements or radicals.

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Synthetic Tanning Agents. Brit. Pat. 157,856. CHEMISCHE FABRIKEN & ASPHALTWERKE AKT.-GES., Griesheim-on-Main, Germany. Jan. 10, 1921. *Sulphonic acids.*—Synthetic tanning-agents are prepared from tars or tar oils by converting the components thereof into phenols by sulphonation and alkali fusion, coupling the resulting phenols by appropriate elements or radicals, and solubilizing the products by introducing acid groups; alternatively the acid groups are introduced into the phenols and the metal salts of the products then coupled.

Treating Leather. Brit. Pat. 157,864. C. R. REUBIG, Giessen, Germany. Jan. 10, 1921. Dressed or undressed leather tanned by any process is treated with a solution of sodium sulphide, sodium thiosulphate and hydrochloric, sulphuric or other inorganic or organic acid, the action being accelerated by addition of caustic alkali. The process is stated to soften hard grained or brittle leathers producing a velvety effect also to decolorize or clear stained or darkened tanned or retanned leathers, and may be used for finishing or in preparation for dyeing. It may be used in place of or in conjunction with combined chrome and vegetable or other mixed tanning, and for degreasing dressed or undressed chrome or other leathers, the degreasing effect being increased by the addition of the caustic alkali, preferably caustic soda.

Treating Leather. Brit. Pat. 157,929. H. BURGER, Frieburg, Baden, Germany. Jan. 10, 1921. Naphthalene or a member of the naphthalene group of equivalent value, either alone or in conjunction with currying substances dissolved therein, is employed for soaking and dressing, impregnating or currying leather. Fat, paraffin, wax, caoutchouc, resin, asphalt, etc., also sulphur and sulphur compounds may be dissolved in the naphthalene. The leather is immersed for half a minute or a minute, being then dried without being washed.

Leather Working Machines. Brit. Pat. 158,832. D. MERCIER, Annonay, Ardeche, France. Jan. 29, 1921. A machine for scraping or stretching hides and skins.

Tanning. Brit. Pat. 159,215. M. BERETTA, Milan. Feb. 21, 1921. Circulation of tanning liquor in tanks through ports by a propelling screw.

Drying Leather Etc. Brit. Pat. 160,197. J. L. FAIRRIE, Liverpool. Sept. 23, 1919. The humidity of gases entering drying-apparatus for leather etc., is controlled by a hygrometer or equivalent which automatically effects the by-passing of part of the moist air leaving the drier to mingle with the entering atmospheric air.

Depiliating Hides Etc. Brit. Pat. 160,435. W. RAUTENSTRAUCH, Treves, Germany. Aug. 4, 1920. Hides and skins are depilated in a barium or strontium hydroxide bath enriched with hide parings, waste, etc., or other albuminous matter, so that the albuminous matter absorbed by the hide from the bath balances or exceeds the loss of hide substance during depilation. The hydroxide is stated to prevent putrefaction of the albuminous matter. A lime bath may be similarly augmented but in this case a suitable disinfectant such as creosote is added.

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W. K. ALSOP . . . . . Editor and Manager
G. W. SCHULTZ . . . . . Associate Editor

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PROPOSED CHANGES IN THE BY-LAWS

Section 9 (b) to be changed to read as follows:

Each class "B" member of the American Leather Chemists Association shall pay an annual fee of $13.50, $10.00 of which shall go to the A. L. C. A. and $3.50 to the Society of Leather Trades Chemists.

Each class "B" member of the S. L. T. C. shall pay a membership fee of $13.50, $6.00 of which shall go to the S. L. T. C., and $7.50 of which shall go to the A. L. C. A.

In addition to the rights and privileges described and limited in Section 7 (a) and (b), payment of the above annual fee shall entitle the mutual member to receive the JOURNALS of each of the two affiliated Associations

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This change in the By-Laws is necessitated by the action of the Society of Leather Trades' Chemists described in the accompanying letter. Under our By-Laws, no change in the By-Laws can be made except at an annual meeting and after three months' notice. While, in consequence, the above change cannot be officially approved before January 1st, it must be sanctioned ultimately if we are to maintain our existing arrangement with the S. L. T. C. for mutual membership. The subscription fees called for on the coming January 1st due bills will therefore be made out on the assumption that the above change has been approved by the Association.

(Signed) H. C. REED,
Secretary-Treasurer.

SOCIETY OF LEATHER TRADES' CHEMISTS

Leather Industries Dept.,
Leeds University, England,
12th September, 1921.

Mr. H. C. Reed,
22 East 16th Street,
New York, N. Y.
My dear Reed,

At the Conference of the S. L. T. C., held in London last week, it was decided in view of the financial condition of the Society, that an increase in subscriptions must take place from January 1st, 1922. The subscription of the British Section was increased from £1.0.0 to £1.5.0 per annum, and the American Mutual Membership subscription from $2.50 to $3.50. When I discussed the question of subscription with you early this year, we had hoped that by increasing the revenue from advertisements it might be possible to continue on the old basis, but we have found that this has not worked out as we intended, and the increased subscription is inevitable. I shall therefore be greatly obliged if you will bring this matter to the attention of your Council, and publish notice of the increase in the *Journal* of the A. L. C. A. at your convenience.

I may add that on more than one occasion at the Conference there were expressions of good-will towards the A. L. C. A., and also appreciation of the valuable committee work that has been carried on by your Association.

With very kind regards, I am

Yours sincerely,
(Signed) D. MCCANDLISH.

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PROPOSED CHANGES IN METHODS

It is proposed to add to the Provisional Methods the following method for the Determination of Free Sulphuric Acid in Leather.

Weigh a 2-gram sample. Add 25 cc. of N/10 sodium carbonate in the case of an unloaded leather (or a larger amount, 35 or 50 cc. in the case of a leather highly loaded with epsom salts.) After careful evaporation to dryness, ignite the contents of the dish until as much of the carbon is burned off as possible. Add 25 cc. of hot water, and digest a few moments. Filter the solution into a 300 cc. flask. Wash the filter paper and unburned carbon well with hot water. Return to the dish and completely ignite. To the remaining ash, add an amount of N/10 sulphuric acid equivalent to the amount of sodium carbonate used, digest for at least fifteen minutes either on the water bath or on a hot plate. Filter into the flask containing the first filtrate. and titrate the excess of acid with N/10 sodium carbonate using methyl orange as the indicator.

(Signed) J. B. CHURCHILL

It is proposed to make the following methods for the analysis of Sulphonated Oils (properly Sulphated Oils) official:—

MOISTURE

Weigh between 30 and 40 grams (depending on amount of water present) into a flask of 250 to 300 cc. and add 75 cc. water saturated xylol, prepared by heating a mixture of water and xylol with frequent shaking and subsequently removing the water in a separatory funnel. Connect to a condenser and place flask in a bath of paraffine or a heavy lubricating oil. Distil moderately until the distillate comes clear. Collect distillate in a tube graduated to 1/10 cc. and wash out condenser with xylol, collecting washings in the receiver also. Place graduated receiver in hot water and when the distillate is clear, cool. The percentage of moisture is obtained by dividing the cubic centimeters of water in the distillate by the grams of oil taken.

NOTE—A graduated tube similar to Eimer and Amend's No. 3812 is recommended for the receiver.

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Ash

Weigh a convenient quantity (from 5 to 10 grams) into a crucible or dish. Ignite gently, allowing the oil to burn and complete incineration at a dull red heat until all carbon is consumed.

Unsaponifiable

Weigh approximately 10 grams of oil into a 250 cc. Erlenmeyer flask and add 50 cc. of an approximately N/1 alcoholic KOH solution. Boil one hour under reflux condenser and cool. Add 40 cc. water and transfer to a separatory funnel. Shake at least three times with petroleum ether (B. P. 40°—75° C.) using 50 cc. each time. Wash ether extract at least three times, first washing to be with slightly alkaline 50 per cent alcohol and the following washings with distilled water. Evaporate ether extract in a tared vessel, dry, cool and weigh.

(Signed) W. K. Alsop, *Chairman* 1917 Committee,
G. W. Schultz, *Chairman* 1919 and 1920 Committees.

It is proposed to alter and add to the Provisional Methods for the Analysis of Sulphonated (Sulphated) Oils as follows:—

Total Alkali

Weigh 10 grams into a 250 cc. Erlenmeyer, dissolve in 150 cc. water (warm if necessary to effect solution), add 30 grams granulated salt, 25 cc. ether and 5 cc. methyl orange indicator and titrate with N/2 H_2SO_4. Calculate to mmg. KOH per gram of sample=A.

Combined So_3

Weigh 8 grams into a 300 cc. Erlenmeyer and boil for 1 hour under a reflux condenser with 25 cc. of N/1 H_2SO_4 (use glass beads to prevent bumping, and shake frequently). Wash the condenser into the flask. To the cooled mixture add about 20 cc. of ether, 100 cc. distilled water, 30 grams of granulated salt and 5 cc. of methyl orange indicator. Titrate with N/2 NaOH Stopper flask and shake frequently during the titration. Deduct

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the amount of H_2SO_4 added from the equivalent of the amount of NaOH required to neutralize and calculate the difference to mmgs. KOH per gram of sample=F.

$$\text{Then per cent combined } SO_3 = \frac{(F + A)8}{56.1}$$

NH_3, Combined and Free Fatty Acids.

Weigh 8 grams of the sample into a 500 cc. beaker, add 50 cc. of 95 per cent alcohol and several drops of phenol phthalein indicator. Run in N/2 NaOH until end point is reached; boil gently until no more NH_3 is given off (to be tested for, with moist red litmus paper), cool, add N/2 NaOH again until the pink color persists; again boil to drive off any remaining NH_3 and add N/2 NaOH after cooling to bring to end point. Record the total number of cc. of N/2 NaOH required. Add 150 cc. water and 5 cc. methyl orange indicator and titrate to acid end point with N/2 H_2SO_4. The number of cc. of N/2 H_2SO_4 required for this titration, corresponds to the combined and free fatty acids. Calculate to mmgs. KOH per gram of sample=(B). The number of cc. N/2 H_2SO_4 minus total number of cc. of N/2 NaOH used to make alkaline corresponds to the alkali minus NH_3 (in the case of the presence of ammonium salts this may be a minus quanity). Preserve the sign and calculate to mmgs. of KOH per gram of sample=(C)

$$\text{Then per cent } NH_3 = \frac{(A - C)1.703}{56.1}$$

B=combined and free fatty acids expressed in mmgs. KOH per gram

B—A=free fatty acids expressed in mmgs. KOH per gram.

Other results to be computed from data obtained above.

Per cent neutralized combined SO_3=1.49× (Per cent combined + 2C], when 2C> (F + A) substitute (F + A) for 2C.

Per cent Na_2CO_3 in ash due to excess of fixed alkali=0.0473 [2C—(F+A)], when the term [2C—(F+A)] is negative there can be no carbonate in the ash.

Per cent salts and impurities in ash =Ash—0.0634 [(F+A) +2C]—0.0473[2C—(F+A)]

Per cent neutralized combined SO_3 = 1.49 × (Per cent combined SO_3)

Per cent sodium bound as soap=0.041 C

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Total Fatty Matter

Total fatty matter is to be taken as the difference between 100 and the sum of Moisture, Ash, Unsaponifiable, NH_3, Sodium as Soap, Neutralized Combined SO_3 and Salts and Impurities.

Neutral Fat

Calculate the free and combined fatty acids -B- to per cent oleic acid and deduct from total fatty matter as found above and call the difference neutral fat.

(Signed) W. K. Alsop, *Chairman* 1917 Committee,
G. W. Schultz, *Chairman* 1919 and 1920 Committees.

THE RELATION OF SOUTH AMERICA TO THE LEATHER INDUSTRY*

By George A. Kerr

In dealing with a subject as broad as the one indicated by the title of this address, it is to be remembered we are discussing a continent of vast area, inhabited by many peoples, ranging in climate from the tropics to the Antartic, and in topography from the greatest mountain and river systems in the Western Hemisphere to alluvial plains, perhaps only rivalled by those of North America or Central Russia.

It is rather difficult to convey within small compass a mental picture of South America as a whole, but in order that its industrial potentialities, and particularly those pertaining to the leather industry may be more clearly realised, an attempt to do so seems desirable,inasmuch, as the dominant physical features of a country or continent have a direct bearing upon its industrial aspects as well as upon the characteristics of its people.

Since the beginning of what might be termed the North American commercial invasion, and the consequent prominence given it through the press, discussion of South America and its trade possibilities have enlisted widespread interest, a very noticeable feature of these discussions being the tendency to treat the whole continent as a unity, this no doubt arising from a habit of thinking of North America as such. If, however, a fair comprehension of South America is to be gained, a brief analyses of its composition is indispensable.

*Read at the 18th Annual Meeting at Atlantic City, June 9, 1921.

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In the first place, politically, it is divided into ten independant governments, and one small group of dependencies—the Guianas —these independent countries are republics in form, and though in a general way similar in ideals, ambitions and outlook, as publicly expressed, there exist many underlying differences which in developing commercial or other relations cannot be ignored.

Methods of intercourse applicable to Peru, are not adapted to Argentina, nor are those of Brazil to Chili, and so on. Commonly the peoples of these countries are spoken of as Latin-Americans, but only in a sense is this true, for all South Americans are not Latins any more than the inhabitants of North America are Anglo-Saxons.

Linguistically Spanish is usually regarded as the universal language, but the fact is that only about one half of the population are on speaking terms with it, the other half speak and use Portugese or have not yet fully emerged from the aboriginal Indian tongues, even South American Spanish varies a good deal, a Chilian may easily be distinguished from his neighbor of Peru, Argentina, or Bolivia, by both pronunciation and idiom; it is therefore well for anyone who contemplates establishing commercial relations to bear in mind, that in the transaction of business, a recognition of these differences is extremely useful in distinguishing the governing traits of the people.

A working knowledge of Spanish is essential to success in all of these countries except Brazil, but preparation to meet all comers involves much more than that; to Spanish should be added French and Italian and, if one hopes to do business in Paraguay intelligently and with the feeling of comfort which perfect understanding gives, Guanani would best be included in the repertoire. The effect of two parties trying to discuss a contract for instance, the one using North American Spanish and the other French, Jewish or Armenian Spanish can be better imagined than described.

In dealing with the South American people. the situation will be found analogous to that existing in the United States, for immigration has brought together as great a diversity of population, especially in the larger centres, as can be found anywhere in this country. This is notably true of Argentina and Brazil, they being not only the two most important countries in extent

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of territory, but also those which have attained the greatest degree of development and possess in a marked degree the material attractions most suitable to the immigrant of small capital.

The population of South America, except for a fringe along the seaboard is very sparse and, does not appear to be increasing rapidly, which is perhaps due to the greater portion of the continent lying within the tropics, a circumstance which will always act as a deterrent to immigration such as the United States has experienced for, until latitude 25° S is passed, (going south) the climate and physical conditions are not conducive to the perpetuation of the activity and enterprise of the peoples of northern latitudes.

Brazil with an area nearly as great as that of the United States. has after four hundred years settlement a population estimated with some liberality at 27 millions, consisting to a great extent of Portugese, negro, and Indian blood, both pure and mixed, this notwithstanding her resources in diversity and magnitude are only second to those of North America. Even Argentina. though it may be termed the white man's zone of South America, is making very slow progress towards peopling her vast expanses of fertile land. With a population of between seven and a half and eight millions there is unlimited room and opportunity for immigrants, especially those who are adapted for agricultural and pastoral pursuits. To-day, however, the tide of immigration has practically ceased to flow and, last year the exodus exceeded the entre. Unfortunately for all of the South American countries, the basis of progress which lies in a spirit of pioneering and, the land hunger so inherent in the Anglo-Saxon does not exist to any marked extent in the emigrant from Southern Europe and, it is from that quarter of the world South America has acquired her new blood.

While marked by the same general tendencies, the peoples of the other countries are not nearly so cosmopolitan as those of the two referred to, and are more truly Latin-Americans, *i. e.* if by that term is meant a people of mixed blood, *viz.;* the Spanish with the original Indian. Immigration to these countries can scarcely be said to exist. such aliens as are domiciled, being to a great extent representatives and employees of foreign companies, business houses and banks, therefore any increase in population

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which may accrue is the result of natural growth rather than exploitation of their resources. Though Latin-American may be correctly applied in describing the natives of the South American countries, of Spanish and Indian blood. it should be borne in mind that as between one country and another, outstanding differences in their characteristics exist, the prime cause probably originating with the decent from Indian races possessing widely differing traits.

The desire to live in the larger cities is, also expressed throughout the continent, as strongly as elsewhere, a sentiment which is liable to hinder the development of vast dormant wealth.

Argentina is a striking example of this, although other countries differ only in proportion to population and urban temptation. One fourth of the whole population of Argentina lives in the city of Buenos Aires, and the ten largest cities and towns contain over 36 per cent. This perhaps would not be an exceptional ratio if the country were an industrial one, but its cardinal resources being those of the ranch and farm, it is remarkable, and not a particularly happy augur for the future of regions promising possibilities so boundless as to strain the imagination, and which only awaits the hand of man to convert it into a land flowing with milk and honey.

The relations of South America to the leather industry assume many aspects, to treat which comprehensively, would require a volume, therefore the speaker's efforts will be directed to submitting as concisely as possible a bird's eye view of what this continent is doing for the world's leather needs.

Before proceeding it is to be noted, the subject is being presented as nearly as possible, as of the conditions existing at the outbreak of the war. Since 1914 the situation has been so abnormal that data reflecting the commercial activities of the past six years cannot be accepted as a permanent condition; at the same time, it should not be assumed readjustment will result in a complete recession to the pre-war status.

More or less manufacturing development has been forced upon some of these countries owing to the impossiblity of obtaining indispensable articles elsewhere, therefore a mild industrial reaction is a natural consequence. Four years famine of imported

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goods proved a rather unpleasant reminder of South America's dependance upon the outside world for almost everything except food.

Once however, back requirements are caught up with, a return to something more nearly a pre-war status than the conditions of 1918—1920 is a certainty, therefore a review from a 1912—1914 standpoint will be a more reliable guide to future expectations than the recent years of super-production and super-purchasing.

South America is to-day, essentially a land of raw materials, and in regard to leather manufacture is pre-eminently so. Of the eleven countries which comprise the continent—the Guianas being counted as one—nine produce cattle, sheep and other live-stock contributing to the needs of the leather industry to the extent of being exporters of hides and skins.

The other two, *viz.;* Peru and the Guianas, so far as known contribute little if anything more than the hides and skins of live-stock imported from neighboring countries for slaughter. Of Peru it may be said there are more or less remote possibilities for the development of cattle raising, as that part of the country embracing a portion of the Amazonian water shed. and bordering on the grazing lands of Brazil, Bolivia, Columbia and Ecuador undoubtedly consists of similar areas, but for the present Peru's beef supply is largely imported. This is also true of Chili, so far as beef cattle are concerned, for though she takes third place in South America in sheep raising, she still, imports much of her beef on the hoof from Argentina, the cattle being trooped over the Andean passes, which in itself is a feat worthy of note, and comparable to driving cattle from one of our western states across the rockies to California. As showing the hardihood of the native South American steer, there is one route between Argentina and Chili where cattle travel for a week or more without sustenance other than water.

Chili, a country one thousand miles long and forty wide, presents too limited a field for cattle raising on a large scale, indeed it is not until a temperate climate is encountered south of Valparaiso that vegetation is sufficiently plentiful to supply local needs. Chilian sheep raising is confined chiefly to the extreme southern territory of Tierra del Fuega, where the climate

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is too cold and bleak and. the pasturage too sparse for profitable cattle grazing, and if one may judge from the way the grass struggles scatteringly in tufts and patches, through endless drifts of stone and gravel, in the chill of an almost perpetual tempest, sheep must be quite dextrous to eke out an existence. Great areas are necessary to maintain flocks, and normally the lot of the sheepmen of southern Chili or Argentina is not an enviable one.

They say until war broke in 1914 a mere existence was about all there was in it, from then until 1919 inclusive, however, the wool growers became veritable Jasons and found their golden fleece as during that period, more than one cleared sums running into seven figures.

Argentina, as a source of raw materials for the world's leather industry, takes first place by a wide margin. From the time of the Spanish conquest, this section of South America has been noted as a pastoral country. Consisting for the most part of an unbroken rich alluvial plain, extending from the Atlantic to the Andean cordillera, the great pampas or prairies have afforded unexcelled natural feeding and breeding grounds for live-stock of all kinds. Grass is prolific the year round and, the devastating winters of the northern continent unknown. Uniformity of climate has proven conducive to rapid increase of the herds, which until comparatively recent years, experienced almost entire freedom from disease and, the other vexatious losses and problems experienced by stockman in more severe climates.

In this connection, it may interest tanners to know that during the past few years the prevalence of foot and mouth disease and anthrax have assumed serious proportions. It appears that foot and mouth disease, while always endemic to some extent was not fatal, cattle so afflicted recovering within a few weeks, in fact a fatal result from this cause was so rare as to invoke comment, recently however, it seems to have become quite virulent and fatal, the losses reported from this cause running into hundreds of thousands of cattle annually for some years past.

Anthrax, unless steps are taken to inoculate with anti-anthrax serum in April or May, breaks out each year in one place or another during July or August, and heavy losses result, in sections where the serum has not been used. Here the speaker may say he

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has found the serum prepared in Argentina very effective as a preventative.

Until forty or fifty years ago, great uncounted herds roamed these fenceless plains, in a manner reminescent of the old days, in the southwest of this country, the stock being altogether native or creolla, *i. e.*, decended from that brought over from Spain in the early days of the Spanish settlement. With the advent of British breeders, alfalfa, and the frigorifico, great changes have taken place, until now herds comprising the aristocracy of live-stock are the rule rather than the exception, the Creolla having been relegated to the natural grass lands of the pampas in the more remote provinces and territories.

The introduction of the frozen meat industry in 1877 gave a great impetus to stock raising in Argentina, and is largely responsible for the remarkable development which has since taken place. Here it is interesting to note Argentina was the first country in the world to export frozen beef, and so put an end to the days when cattle were killed in South America for the hide rather than the beef.

In 1913 the best estimates put the number of cattle in Argentina at 29 millions or exactly the same number reported by the 1908 census. During these five years, the consumption of cattle for export beef appears to have kept pace with the production, as the reported slaughter rose from 1,800,000 in 1908 to 3,750,000 in 1913. That the maximum yield without depletion of stock or feeding herds had been reached before this is indicated by the increased slaughter of cows, the proportion rising from 23 per cent to 40 per cent of the total.

During the war the excessive demand for frozen and canned meats resulted in extensive inroads being made upon stock and breeding herds, and packers eagerly sought new sources of supply. That the new sources did not meet the anticipations seems to further corroborate the opinion that the maximum available supply of cattle for slaughtering purposes had been reached prior to 1915 not only in Argentina but elsewhere. Under these circumstances, any material increase in the volume of hides available for export from South America need not be expected for some years.

The figures given above only indicate the hides taken off in

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the large centres of consumption and for export beef, but there is a very considerable take off in the rural districts of which no account is taken. A great proportion of these hides do not find their way to tide-water, being absorbed by the many small local tanneries, on the ranches etc., where raw hide takes the place of leather, rope, and cordage, nevertheless a quarter of a million hides from this source may be counted on as available for the foreign market, therefore the annual volume of hides which Argentina contributes to the world market may be put at 4,000,000 annually. This estimate is in keeping with the annual yield of beef cattle.

Of the hides exported, about two thirds are green salted, and one third dry. Recently over 60 per cent has been coming to the United States, the remainder going to Europe. The destination, however, seems to fluctuate considerably, as for instance in 1913 Germany took over one half of the total, whereas in 1914, and, before the war had seriously affected German imports, the United States took the major portion, the positions of these countries as purchasers of Argentina hides being almost exactly reversed in one year.

As a sheep growing country Argentina occupies a place of great importance, this phase of live-stock production being conducted more or less throughout the entire country south of the province of Buenos Aires inclusive. A total of 80,000,000 sheep was claimed for 1913 and although a great and unexplained shrinkage is reported a few years later, the greater estimate is rather confirmed by the clip of wool. While wool-growing is the prime motive for raising sheep, the establishment of extensive packing houses in Southern Argentina has made a considerable supply of sheep skins available. In 1914, 29,000,000 pounds were exported, of these France took 90 per cent, the remaining 10 per cent being scattered over seven other countries.

In a country possessing one and a quarter horses for every man, woman and child in it, *i. e.*, about 9,000,000 horses it would seem horse-hides would constitute a considerable item of export, but in 1914 this amounted to only 3,000,000 pounds. During this year a like volume of goat skins were also exported. the bulk of them coming to the United States.

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Brazil, the greatest of South American countries, territorially and in population, ranks next in importance to Argentina, although the development of stock raising, and hence a source of hides and skins, is in no manner proportionate to the latter. A good start has been made in this direction, which if steadily pursued, will put Brazil in a leading place. Possessed of vast areas of natural grass lands, many of which have not yet been fully explored, the foundation for a great pastoral industry lies within her borders.

It is true the less favorable geographical position of Brazil will make for slower progress, as proceeding from the tropical and sub-tropical climates, are serious difficulties in the way of raising high grade stock, such as growing fattening grasses comparable with Argentina's alfalfa, prevention or eradication of tick etc., etc. Important steps towards accomplishing all of these aims have been taken within recent years, notably by the Brazil Land & Cattle Co., a North American concern, which guided by the ability and indomitable effort of Murdo Mackenzie has made marked progress.

Of the twenty Brazilian states, nine carry cattle to the extent of one million or more, the most important of these are, Rio Grand do Sul with 8,500,000, Minas Geraes 7,000,000, Goyaz 4,500,000 and Matto Grosso 3,750, 000, the total for the country, it is claimed, being 37,000,000.

These figures would seem to refute Argentina's claim to first place as a producer of hides for export, but it is as a source of raw material for the outside world these countries are being ranked, it therefore must be taken into consideration the population of Brazil is said to be 27,000,000 against Argentina's 7,500,000, the ratio of cattle per capita being 1.4 head for Brazil and 3.85 for Argentina.

From this it follows the home consumption at the present time absorbs practically the entire yield of beef cattle, the estimates showing that of an annual yield of 4,650,000 head, 4,500,000 are consumed and only 165,000 are available for export beef. The quantity of hides available for export are not of course governed by the number of surplus cattle, but it is very materially

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affected by the needs of the greater population, and also by the great wastage—which is enough to make a tanner weep—due to the lack and cost of transportation. According to the most reliable information obtainable, about 2,500,000 or approximately 50 per cent of the total take off were exported.

The classification of Brazilian cattle is of some interest to the tanner, inasmuch as the character of the hide produced, is largely a question of the animal producing it. Of the 37,000,000, 19.000,000 are native stock and though said to comprise at least five varieties, they are not sufficiently distinctive to be distinguished from a hide standpoint; 8,500,000 are of European stock in varying degrees of mixed breeding, the imported blood being chiefly Hereford, Angus, Devon, Jersey, Swiss and Dutch.

Unless it is for breeding and dairy purposes, pure bred herds scarcely exist, and high grade stock is not likely to become a factor until grazing conditions are modified by replacing to a very considerable extent the indigenous grasses by others better suited to its more delicate requirements, high grade animals not possessing the hardihood of the native which are very much on the order of the Texas longhorn of past days

The third class is the Zebu or Indian stock, of which it is claimed there are 10,000,000. Many years ago this breed was introduced by some enterprising Englishmen as being immune to the troublesome tick or garapata, it was thought cross-breeding with the native strains would render the stock immune. Their anticipations were realised to some extent, but like many other good things, it was not an unmixed blessing, as it was found conformation, both as to beef and hide deteriorated to an extent which affected the value of both. Attempts are now being made to eliminate Zebu blood, but the strain is very persistent and, the outcrop of hump and narrow quarters so characteristic of the Zebu is conspicuous in almost every native herd. In this connection, Argentina has prohibited the importation of this class of cattle, and although stockmen are not in unamimous agreement with the policy, it seems obvious, the best grades of beef and hide stock must be free from anything savoring of the sacred ox.

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At present Brazil is of no importance as a sheep raising country and, it is doubtful if she ever will be, unless it is in the southern province of Rio Grande do Sul.

Uruguay next claims attention as a hide and skin producing region and, though the smallest country of South America, its importance cannot be classified by its area or population, here development and progress equal that of Argentina, and surpasses all others, in fact Uruguay may be said to be an intensified miniature replica of her greater neighbour across the river.

In general characteristics and, from the hide and leather point of view Uruguay resembles Argentina so much that detailed description would be superfluous, it should be observed, however, this remarkable development is largely due to her favorable geographical position, climate and, the faculty which the Uruguayan possesses for getting along with English speaking peoples.

When one first contemplates her wealth of live-stock in comparison with the countries possessing much greater grazing areas one naturally accepts the figures with a grain of salt, but while in common with South American statistics in general, those of Uruguay do not err on the low side, she is none the less, the most remarkable of South American countries in this respect.

After making due allowances Uruguay may be credited with 7,750,000 cattle, 11,500,000 sheep and some 300,000 hogs, this latter being an infant industry for the present. Some estimates have put the sheep at 27 or 29 millions but this is obviously a much exaggerated figure.

In 1914 approximately 730,000 cattle and 310,000 sheep were slaughtered by packers, saladeros, and jerked beef works. During 1917—18 the number of cattle so slaughtered increased by 33 per cent, while the number of sheep killed decreased to a like extent.

With regard to hides exported, there is some difficulty in arriving at the exact quantity, for instance, we find with a total take off of about 1,500,000 in 1917 nearly 1,750,000 hides were said to have been exported. The excess may be accounted for by the shipment of accumulated stocks or the re-exportation of hides arriving in Montevideo from other sources. Perhaps

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the most reliable estimate of Uruguay's annual hide resources is that based upon the yield of animals suitable for slaughter, this would be, about 1,250,000, or after deducting for home consumption and wastage, 1,000,000 in round numbers. This estimate may seem rather out of line with the reported take off for 1917 and 1918, but it should be remembered that during these years the take off was much in excess of production.

There now remains what may be classed the minor group of cattle or hide producing states, they are five in number, *viz.*; Paraguay, Venezuela, Columbia, Bolivia and Ecuador.

The first three of these countries are about on a par, both as to volume of hides available for export and future possibilities. Bolivia and Ecuador are still in the making, both export hides to some extent, in somwhat roundabout ways, but neither can be considered as likely to prove influential sources until their transportation problems have been solved.

As being the most progressive and, also a recently selected field for exploitation by North American capital, Paraguay is entitled to first place among these minor countries in the way of stock raising a position she will probably maintain as long as the government remains fairly stable and liberal in its policy to foreign capital. At the present time the country carries about 3,000,000 cattle or a comparatively slight margin above the requirements for home consumption, that is to say not more than 150,000 to 200,000 head per annum are available for freezing or conserving purposes, the domestic slaughter being from 300,000 to 350,000. In 1914 268,000 hides were exported, that is slightly less than 60 per cent of the total take off. Of these 196,000 were salted hides and 72,000 dry. Since then there has undoubtedly been some increase, owing to the establishment of several packing plants, but it may be safely assumed that for years to come the available hides will not exceed 450,000 to 500,000 per annum. These are almost entirely from Creolla or native stock, as except in the south where Argentina and Uruguyan influences towards better grades of cattle have made some impression little has been done in this direction. American investors are making some attempts, but what has been said of the difficulties met with in introducing high grade strains into Brazil, applies equally to this remote inland state.

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Regarding Venezuela as a cattle country, it may be said to have attained a measure of prominence somwhat out of proportion to its performance. Venezuela's proximity to North America, and being on a much travelled tourist route has probably led to greater advertising of its reputed cattle resources, than the more remote countries have been favored with. It is true the great llanos of the Orinoco basin, which are analogous to some extent to the pampas of Argentina, and the chaco region of Paraguay and Bolivia afford great possibilities, which still remain to be taken advantage of, and it is more than doubtful if there are 3,000,000 cattle in the country; in any event it is certain the frigorifico established some fifteen years ago has never been able to operate for a continuous period at anything like capacity owing to a shortage of cattle within transporting distance. With regard to the future it would appear there are prospects for a material extension of the cattle industry as governmental action has stopped the indiscriminate slaughter of cows and stock under two years old; increased herds will likely result, especially if recent prices are maintained. The stock of Venezuela like that of Paraguay is native and, partakes of the same general characteristics, the hides weighing on the average about 65 pounds salted and 22 pounds dry.

Judging from the domestic consumption of beef, the total take-off of hides does not exceed 500,000 per annum, of these not more than 150,000 find their way to the foreign market, the balance being utilised at home or lost as wastage, which no doubt is very great owing to the absence of transportation facilities.

Colombia, a country whose rank as a hide producer has not yet become of great importance, possesses possibilities, which have attracted considerable attention during recent years, and a packing house is being. or has just been erected near Cartagena. Besides this enterprise the United States government frigorifico at Colon or San Christobal has drawn to a great extent upon Colombia for its supply of live stock. At the present time the country carries from 1,500,000 to 2,000,000 head of cattle, with an annual take off of hides approximating 300,000 about one half of which are available for export, and which come almost wholly to the United States.

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In point of actual knowledge, less perhaps is known of Bolivia's cattle resources than any of the preceding countries; that a very considerable portion of the country is adapted for stock raising we do know, and also on the grazing lands east of the cordillera there are quite large herds of cattle, but the development of this region will be slow, as it is from a transportation standpoint the most inaccessible in South America.

Any attempt to estimate the number of hides coming from Bolivia would be futile, as such as find their way out, do so in several directions; some come down the Paraguay river, others go to the west coast and, on the north and east they pass through Brazil, to a large extent upon hoof.

Ecuador has been referred to more on account of its future possibilities than for its present importance. A recent survey claims the country to be capable of supporting millions of cattle, upon its cooler uplands, it is certain however that it does not carry to exceed300,000 at present, and produces no surplus over domestic consumption.

Summing up South America's hide resources, it would appear that of a total take off of 13,750,000 about, 8,400,000 are available for export. Any figures on world production of hides are necessarily derived to a certain extent from individual estimates and therefore are as much a matter of opinion as actual knowledge, further the cattle industry seems to be subject to great and unaccountable fluctuations, so that no one year's productions can be taken as a criterion for an extended period. Utilizing the best information available, it would appear that South America contributes about 15 per cent of the leather industry's consumption of cattle hides, and a slightly greater proportion of sheep-skins.

It is the future potentialities of the southern continent to produce hides and skins, which is of greatest interest to the tanner and with the exception of Africa, it may be said no continent compares with South America in this respect. That many times the number of cattle now existing can be maintained is quite evident, and by the adoption of intensive methods, it is difficult to say to what extent the industry could be carried.

Progress will be governed by the usual factors of supply and demand, the extension of transportation facilities and, the increase of land values.

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Just at present the frozen and chilled beef industries appear to have developed more rapidly than the supply of live-stock, and considerably in advance of the normal demand for their products. The stimulus of war requirements accounts for this condition, and though the war has developed a permanent increased consumption of beef in Europe, there is little reason to expect a largely increased supply of hides from South America in the near future.

Tanning Materials

Tanning agents being second only to hide substance in the production of leather, South America's place as a purveyor, present and prospective, of vegetable tanning materials is worthy of more than passing notice. Four countries, *viz.;* Argentina, Paraguay, Venezuela and Colombia produce for export, crude and manufactured tanning materials, consisting of quebracho wood and extract, mangrove bark and extract, divi divi and algarrobilla.

The tannin bearing plants and trees indigenous to the continent are by no means confined to these varieties and while not as yet produced for export, several of them are in common use in the local tanneries of the various countries. So far as the speaker's knowledge goes, none of them equal the materials above mentioned in tannin value, and it is for this reason they have not thus far appealed to the manufacturer of extracts.

Quebracho, in comparison with other South American materials stands alone in quantity available and, general all round utility and value, and taking into account the great area of the quebracho forests, it will probably be many years before the less valuable materials attract more than local interest.

In a recent article, the speaker treated of the quebracho forests of Argentina and Paraguay, therefore further reference may be omitted at this time, however, the development of the tanning extract industry of these two countries is of interest as showing the extent to which the leather industry at large has come to depend upon them for its tanning material. There are in Argtina some twelve plants with an annual output capacity of approximately 125,000 metric tons of solid extract, and in Paraguay, five plants with a combined capacity of about 50,000 tons, making a total of 175,000 metric tons available for foreign consumption annually. Since 1914 the production capacity has been increased 50,000 tons more or less, by the addition of five new plants, in

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which are included the relocation of one plant removed from Paraguay, and the concentration of one or two somwhat dormant plants in Argentina. With regard to the total capacity of 175,000 tons, it should be said the maximum output for a whole year has never been attained. as the factories comprising the two groups, have rarely, if ever, all operated simultaneously for any length, of time, and although the demand was extremely active during, and, for some time after the war, lack of ocean transportation and, in Paraguay, of raw material held production to about normal. Production was also curtailed by the compulsory dismissal of the German staffs operating the plants, and the failure of those who took their places to increase the output. Since transportation became available, labor complications have seriously interfered with continuous operation, hence the actual production of the last year or so has not materially increased over that of 1914, and to hazard a prognostication, I may say, unless South American labor becomes more stable. (the prospects for which are not overly good), a return of the leather industry to normal conditions in the near future, would probably be met with an inadequate supply of quebracho extract.

In 1914, 80,000 metric tons of quebracho extract were exported from Argentina and 11,000 tons from Paraguay, 91,000 tons in all. Of this total Argentina furnished 90 per cent of her production capacity, and Paraguay 40 per cent of hers. In this connection it may be noted, the small output in Paraguay at this time was wholly a matter of inability to compete with the more favorable conditions of Argentina. On its face, it would seem the capacity for producing extract in these countries is greatly in excess of the normal demand, but it should be remembered that until 1914 large quantities of logs were exported for conversion elsewhere. During that year 292,000 tons of logs were shipped to Europe and the United States, in terms of extract this is equivalent to 75,000 tons, thus it is apparent the world consumption of this material was then about 166,000 tons, or rather less than the present nominal capacity for production.

This condition would make the resumption of quebracho extract manufacture in Europe seem unnecessary and illogical, which as a matter of fact it has been since its value as a tanning agent was permanently established.

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As to the future, it may be observed, that at the present rate of consumption, there is ample quebracho timber to last for over seventy-five years, after making due allowance for that required for other purposes.

Compared with quebracho, the mangrove, divi divi and algarrobilla of Venezuela and Colombia are of very secondary importance. The exports of mangrove bark from these countries has seldom exceeded 20,000 tons per annum, and will not increase much until a well financed and organised effort is made to develop its production and use; aside from this, there seems no good reason why South American mangrove should not successfully compete with that of the East Indies. So far as known, no attempt has been made in Venezuela to manufacture mangrove extract, but there are two small plants in Colombia, one at Cartgena, the other near the mouth of the Sinu river, some seventy miles west. Neither of these plants have been altogether successful, owing chiefly to the crude methods and apparatus employed, and also to the difficulty of obtaining nonsaline water. There is also some difficulty in securing a supply of raw material, as the native labor finds more congenial means of sustaining life than working in mosquito infested mangrove swamps.

Such bark as is or has been brought to the factories referred to, varies greatly in tannin content and quality, little attention evidently being given to the selection of the better varieties. That there are great quantities of mangrove bark in both countries seems well confirmed, but a thorough expert investigation is necessary before the prospective value of the mangrove tannin industry could be reliably estimated.

The production and export of divi divi and algarrobilla seem to have attained a stationary point, as the exports which vary from year to year, according to the season, do not average much over 10,000 tons annually, the quantity being about equally divided between the two countries. Both of these crude materials are peculiarly susceptible to climatic conditions and, liable to discolor and decomposition from moulding, thus considerable quantities are lost to the market. To secure a uniform product and develope their use to the utmost, these materials should be manufactured into dry extract at the source of supply.

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It might be inferred that Brazil with her great forest resources would eventually develop to be a factor in the supply of tanning materials, but so far as can be ascertained, no especial survey in this direction has been made; much of her forest territory has not been explored, therefore it is useless to conjecture what future stores may be drawn from this unknown region. That there is tannin bearing vegetation to some extent goes without saying, but whether an area as rich as the quebracho forests to the south exists, is more than doubtful. At present such modern tanneries as there are in Brazil import and use quebracho to a large extent.

With regard to the other countries, they all possess tanning materials to a greater or less extent, and apparently in sufficient quantity to provide for their domestic requirements, there has been no effort, however, to exploit them for foreign consumption.

Important as the South American continent is now as a purveyor of tanning material, there is little doubt it will become increasingly so, and now that the policy of conservation has taken root many generations will come and go before this great contribution to the world's necessities wanes.

Production of Leather

Having outlined the relation of South America to the leather industry as to raw materials, this address would not be complete without a brief glance into the leather or finished product side of the question.

As to the volume and value of leather produced, let me say at the beginning, no one in any degree familiar with more than the seaboard districts of the continent would hazard a guess. The most that can be said in this respect is, that the necessities of the population are largely provided for by the domestic production and so far there has been no surplus for export, except perhaps in an intra-continental way. Travelling through the inland parts of these countries, the art of tanning strikes one as being indigenous and obiquitous. Once the greater centres of population are left behind, there is scarcely a village or estancia that has not a Simon among them, who produces astonishingly good good leather of different kinds by methods reminescent of mediaeval Spain, for in common with other industrial arts as practised in these rural sections, tanning is very much where the conquistadores or Jesuit fathers left it two centuries ago.

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Outside of the urban centres, the needs of the people are few and simple, raw hide serving many purposes for which leather is used in other countries and, as the feet of at least two thirds of the populace never have known a shoe, the consumption of leather is extremely limited. In the more developed countries there are a few modern tanneries operating on a fairly large scale, these plants turn out sole leather chiefly, although I have seen very creditable upper stock, as well as case and bag leather, alleged to be of domestic manufacture.

An idea of the extent to which South America draws upon outside sources for leather and leather goods may be gathered from the imports, although here as with other statistics, too much dependance cannot be placed upon the figures so reported, but basing an estimate upon those submitted by the better organised countries and, the fact that South America is not a heavy consumer of leather, it is reasonably certain not to exceed ten million dollars gold per annum is spent on foreign leather and leather goods.

The total importations for the continent are normally in the neighborhood of nine hundred million dollars, therefore importations of this class constitute only 1.1 per cent of the whole. Allowing that the population is forty-five millions with a purchasing power of $20.00 per capita for imported goods, the proportion spent on imported leather, crude and manufactured is the insignificant sum of 22 cents.

It should not be concluded from this that the field for foreign goods is susceptible of great immediate expansion, as in the first place there will have to be a very material advance in the standards of living of the masses,or an important influx of people whose standards demand shoes and other conveniences of leather, before any noticeable increase in the consumption ensues.

That there are signs of advancement in the demand for better foot gear and clothing among the laboring classes is evident; wages have already materially increased, and with the almost complete unionising of all classes of labor will, most likely be maintained. With money in their pockets over and above that required for food and housing, there is little doubt, but that the leather shoe will displace the rope soled alparagata or bare feet before long. However, in the light of recent developments it

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appears probable any increased demand will be met with domestic production; shoe manufacturing is becoming well established throughout the continent; Argentina already boasts 200 shoe factories with capacities ranging from a few hundred to 2000 pairs per day. Brazil possesses several up to date factories and Chili, Peru and Venezuela have also entered the field. On the whole it seems likely, the expansion of the leather industry in South America will depend very largely upon outside capital or, capital in the hands of Europeans and North Americans domiciled there, as the true Latin-American as a rule is not attracted by industrial investments, preferring the more easily won and greater returns afforded by his ancestral pastoral and agricultural resources.

That the continent possesses all the elements, both material and physical to give it a leading place in the leather industry of the world there is no doubt, but before reaching it, there are other factors to overcome. Of these the most important are stability of finance and labor, the abolishing of export duties, and permanence and continuity of liberal governmental policies, calculated to foster industrial expansion. With these assured, the great anxiety of the South American republics to exploit their raw material resources industrially, and convert them into finished products at the source, will no doubt meet a ready response from outside capital.

THE EFFECT OF ATMOSPHERIC HUMIDITY ON THE DETERMINATION OF MOISTURE IN LEATHER*

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Concordant, accurate results are quite as difficult to obtain in determining moisture in organic materials as in determinations involving chemical reactions and separations. Moisture results by different analysts on identical samples have differed quite as widely as results on other constituents. The same analyst has not always been able to duplicate his results, and on repeated drying of the same charge fluctuating results were obtained, partly ex-

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plained as due to oxidation or to loss of volatile constituents other than water.

While it is quite generally recognized that both relative humidity and temperature affect rate of evaporation and the drying of solids, little if any attention has been given to the effect of relative humidity and temperature on the determination of moisture in materials or indeed on their effect on other analytical determinations.

The conviction has been growing on the workers in this laboratory that the relative humidity of the air of the laboratory during the drying, cooling and weighing of the sample has more or less effect on the results of any analytical determination, especially of those involving the drying and weighing of considerable quantities of organic matter as in the case of determining moisture in such materials. The results of this laboratory in the collaborative committee work of the A. L. C. A. in 1920 on moisture in leather showed material fluctuations upon repeated drying in the combined evaporator and dryer, which it is believed is to be accounted for in this way. This led to a study of the subject, some of the results of which are presented in this paper.

The samples of leather used for this work are sufficiently described in Table I.

TABLE I. DESCRIPTION AND ANALYSIS OF SAMPLES USED FOR MOISTURE DETERMINATION.

Sample No.	Description	Preparation	Grease	Soluble solids	Epsom salts	Glucose
			%	%	%	%
1	Union sole leather	Shredded	4.3	20.6	2.4	1.6
2	Oak " "	Planed	1.5	17.1	0.0	2.0
3	Oak " "	Shredded	3.8	18.2	0.0	0.4
4	Union " "	"	1.7	23.5	2.1	2.5
5	Oak " "	"	2.1	30.9	2.9	7.3
6	Hemlock sole leather	"	1.3	27.6	2.6	7.5
7	Russet harness backs	"	8.2	15.5	0.0	0.0
8	Russet harness strap leather	"	5.9	—	—	—
9	Black harness leather	"	26.2	16.2	2.0	4.5
10	" " "	"	22.5	—	0.0	1.6
11	Unwaxed chrome sole leather	"	—	—	—	—
12	Waxed chrome " "	"	—	—	—	—
13	Vegetable tanned hide powder	—	—	—	—	—
14	Hide powder untreated	—	—	—	—	—

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TABLE II.—COMPARISON OF WEIGHING BOTTLES AND TANNIN DISHES.

Sample No.	Kind of container	Hours of drying				
		16	32	48	64	80
		Moisture %	Moisture %	Moisture %	Moisture %	Moisture %
1	Weighing bottle	9.36	9.50	9 62	9.68	9.58
	Tannin dish	9.51	9.69	9.80	9.98	9.82
difference		0.15	0.19	0.18	0.30	0.34
5	Weighing bottle	10.09	10.31	10.52	10.68	10.53
	Tannin dish	10.35	10.67	10.92	11.15	10.90
		0.26	0.26	0.40	0.47	0.37
% Relative humidity during drying		31	31	31	39	65

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Loosely Covered Dishes or Weighing Bottles. Flat bottomed, rather wide, low open dishes, because of their greater convenience, are usually employed in making moisture determinations in organic materials. Since, however, atmospheric humidity would be expected to affect results gotten in such dishes, more than those gotten in tightly cofered weighing bottles, it was deemed wise to make preliminary tests in both low wide dishes and in covered weighing bottles. The dishes used were the ordinary tannin dishes about 70 mm. wide and 50 mm. high. They were covered with a watch glass on removing from the oven and weighed without disturbing the cover. The weighing bottles were fitted with ground glass covers and were about 45 mm. wide and 65 mm. high. The dryings were made in an electric oven at 100° C. and samples Nos. 1 and 5 were used. The results are given in Table II.

It will be seen that in every case higher results were obtained in the large tannin dishes than in the smaller weighing bottles and while there is no indication that the results obtained in the weighing bottles are more reliable than those obtained in the dishes, nevertheless it was deemed safest to use only the weighing bottles in subsequent work in order to avoid certain possible errors when the loosely covered dishes are used.

The procedure employed in this work was as follows: Weigh rapidly and accurately 5 to 6 grams of leather into tared glass-stoppered weighing bottles having a diameter of 45 mm. and height 65 mm. and dry for 5 hours. When the period of drying is up, quickly place the tops on the bottles and put in desiccators recently filled with fresh sulphuric acid; allow to cool for ½ hour and weigh.

After weighing, the samples remained in the desiccators over night and were dried the following day for 5 hours, desiccated and weighed as described. All samples listed in each table were weighed out and dried at the same time.

Successive Dryings and Different Ovens. Some results on samples 1 and 13, showing the fluctuations in moisture content determined by drying for 5-hour periods from day to day for a total of 75 hours in an electric oven at 100° C.; in a combined

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TABLE III. DRYING IN 3 TYPES OF OVENS AT DIFFERENT HUMIDITIES.

	Sample No. 1			Sample No. 13			
Time of heating Hrs.	Electric oven at 100° C. Moisture %	Evaporator and dryer Moisture %	Vacuum oven at 70° C. Moisture %	Electric oven at 100° C. Moisture %	Evaporator and dryer Moisture %	Vacuum oven at 70° C. Moisture %	Per cent relative humidity
5	8.18, 8.35 — 8.27	8.11, 8.00 — 8.06	7.90, 7.79 — 7.85	13.73, 14.03 — 13.88	13.36, 13.60 — 13.48	12.84, 13.37 — 13.11	66
10	8.49, 8.63 — 8.56	8.58, 8.53 — 8.56	8.45, 8.40 — 8.43	14.12, 14.35 — 14.24	14.05, 14.16 — 14.11	13.82, 13.97 — 13.90	61
15	8.47, 8.61 — 8.54	8.52, 8.40 — 8.46	8.31, 8.25 — 8.28	14.17, 14.34 — 14.21	13.95, 14.01 — 13.98	13.80, 13.83 — 13.82	68
20	8.71, 8.87 — 8.79	8.78, 8.67 — 8.73	8.48, 8.45 — 8.47	14.41, 14.59 — 14.50	14.21, 14.28 — 14.25	13.94, 14.03 — 13.99	49
25	8.84, 8.94 — 8.89	8.93, 8.80 — 8.87	8.70, 8.63 — 8.67	14.49, 14.67 — 14.58	14.35, 14.42 — 14.39	14.12, 14.19 — 14.16	42
30	8.69, 8.83 — 8.76	8.73, 8.61 — 8.67	8.45, 8.39 — 8.42	14.41, 14.60 — 14.51	14.16, 14.22 — 14.19	13.92, 13.94 — 13.93	63
35	8.83, 8.98 — 8.91	8.95, 8.83 — 8.89	8.67, 8.59 — 8.63	14.56, 14.74 — 14.65	14.36, 14.42 — 14.39	14.06, 14.16 — 14.11	46
40	9.22, 9.33 — 9.28	9.18, 9.07 — 9.13	8.90, 8.86 — 8.88	14.88, 14.98 — 14.98	14.64, 14.71 — 14.68	14.29, 14.43 — 14.36	40
45	9.31, 9.44 — 9.38	9.20, 9.12 — 9.16	9.07, 9.00 — 9.04	14.99, 15.16 — 15.07	14.71, 14.77 — 14.74	14.48, 14.59 — 14.54	43
50	9.33, 9.47 — 9.40	9.18, 9.11 — 9.15	9.00, 8.91 — 8.96	15.05, 15.21 — 15.13	14.72, 14.77 — 14.75	14.42, 14.48 — 14.45	45
55	9.36, 9.51 — 9.44	9.12, 9.09 — 9.11	9.00, 8.91 — 8.96	15.09, 15.24 — 15.17	14.73, 14.81 — 14.77	14.41, 14.48 — 14.45	45
60	9.36, 9.50 — 9.43	9.26, 9.18 — 9.22	8.92, 8.84 — 8.88	15.07, 15.24 — 15.16	14.75, 14.82 — 14.78	14.39, 14.41 — 14.40	46
65	9.36, 9.50 — 9.43	9.26, 9.14 — 9.20	8.88, 8.80 — 8.84	15.08, 15.25 — 15.17	14.74, 14.84 — 14.79	14.37, 14.36 — 14.37	48
70	9.30, 9.41 — 9.36	9.11, 9.02 — 9.07	8.78, 8.74 — 8.76	15.02, 15.14 — 15.08	14.63, 14.67 — 14.65	14.26, 14.29 — 14.28	60
75	9.43, 9.59 — 9.51	9.41, 9 31 — 9.36	9.03, 8.97 — 9.00	15.11, 15.24 — 15.18	14.89, 14.94 — 14.92	14.41, 14.50 — 14.46	35
Dif. between duplicates (5 hrs.)-	0.17	0.11	0.11	0.30	0.36	0.47	
Dif. between duplicates (75 hrs.)-	0.16	0.10	0.06	0.13	0.05	0.09	

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evaporator and dryer at 98°-100° C.; and in a vacuum oven at 70° C., are presented in Table III. The average relative humidity of the atmosphere in the laboratory during each period of drying is also recorded.

It will be noted that the greatest fluctuations occurred between the third and fourth, fifth and sixth, and the thirteenth and fourteenth periods of drying. There was also a difference of 19 per cent, 21 per cent and 25 per cent respectively in relative humidity of the laboratory at these times, indicating that the fluctuating results are due to difference in the humidity conditions during the periods of drying. The fluctuations were also shown with the vacuum oven. The average differences in the moisture results for a difference of 25 to 30 per cent relative humidity is practically the same for the three types of drying oven and is approximately 0.25 per cent or 0.01 per cent for each 1 per cent difference in humidity between 35 per cent and 68 per cent.

The table also shows that the highest results are obtained with the electric oven at 100° C., and the lowest with the vacuum oven at 70° C., and further these relations hold throughout the whole drying time. It is also worth noting that the duplicates bear the same relation to each other throughout the whole drying time. The weighing bottle showing the lower result holds this position to the end in all cases.

Electric Oven, 65 Per Cent Humidity. In Table IV are shown some results on the loss in weight by drying samples of leather in the electric oven at 100° C. under a constant relative humidity of 65 per cent at 70° F.

In these experiments where the relative humidity of the air remained constant, closely agreeing results between successive dryings were obtained. There is no fluctuation under this condition, as was the case when the drying was done under the ordinary atmospheric room conditions with varying relative humidity. There is, however, a slight but nevertheless a remarkably consistent steady loss in weight during each successive 5-hour period of drying, and the loss continued apparently after 75 hours drying. These results emphasize the necessity for rigidly specifying the time of drying in determining moisture in leather.

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TABLE IV.—DRYING IN AN ELECTRIC OVEN AT 100° C. AT CONSTANT RELATIVE HUMIDITY OF 65%.

Time of heating Hrs.	Sample Number 1 Union sole Per cent moisture		5 Oak sole Per cent moisture		7 Russet strap Per cent moisture		9 Black harness Per cent moisture	
5	8.77 8.93	8.85	9.58 9.36	9.47	9.09 9.20	9.15	7.41 7.29	7.35
10	8.87 9.00	8.94	9.67 9.32	9.60	9.19 9.30	9.25	7.52 7.45	7.49
15	8.94 8.98	8.96	9.75 9.57	9.66	9.29 9.29	9.29	7.58 7.48	7.53
20	9.08 9.16	9.12	9.93 9.78	9.86	9.27 9.44	9.41	7.69 7.65	7.67
25	9.16 9.23	9.20	10.03 9.85	9.94	9.43 9.52	9.48	7.79 7.71	7.75
30	9.20 9.28	9.24	10.12 10.06	10.09	9.49 9.55	9.52	7.86 7.81	7.84
35	9.20 9.30	9.25	10.19 10.02	10.11	9.50 9.56	9.63	7.91 7.85	7.88
40	9.29 9.40	9.35	10.31 10.13	10.22	9.61 9.65	9.63	8.01 7.92	7.97
45	9.32 9.41	9.37	10.36 10.18	10.27	9.61 9.67	9.64	8.03 7.95	7.99
50	9.38 9.47	9.43	10.49 10.26	10.38	9.68 9.72	9.70	8.06 8.00	8.06
55	9.40 9.51	9.46	10.49 10.30	10.40	9.69 9.74	9.72	8.13 8.04	8.09
60	9.42 9.54	9.48	10.59 10.35	10.46	9.73 9.77	9.75	8.20 8.10	8.15
65	9.45 9.56	9.51	10.60 10.38	10.49	9.74 9.80	9.77	8.21 8.12	8.17
70	9.46 9.62	9.54	10.63 10.42	10.53	9.76 9.82	9.79	8.26 8.16	8.21
75	9.52 9.64	9.58	10.66 10.44	10.55	9.80 9.84	9.82	8.27 8.19	8.23
Difference between duplicates 5 hrs.	0.16		0.22		0.11		0.12	
Difference between duplicates 75 hrs.	0.12		0.22		0.04		0.08	

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Electric Oven, 31 Per Cent and 65 Per Cent R. H. Results obtained by drying several kinds of leather in an electric oven at 100° C. and at 65 per cent and at 31 per cent relative humidity, respectively, are given in Table V. The drying at the higher humidity was done in a constant temperature and humidity room (temperature of room maintained at 70° F.). The lower humidity condition existed in the laboratory where the relative humidity during the four five hour periods of drying was 39, 26, 30 and 28 per cent respectively, and the temperature was between 74° and 78° F.

In every case, without exception, drying at the lower relative humidity gave the higher percentage loss. Taking the results at the end of the 20 hours of drying, the differences are from 0.17 per cent to 0.56 per cent. It is of interest also to note that sample 10 which has a difference of but 0.17 per cent is a black harness leather having a grease content of 22.5 per cent, while sample 12 having a difference of 0.22 per cent is a heavily waxed chrome leather. Sample 11 is the same leather as 12, except that it is unwaxed. After 10 hours drying the difference on leathers containing little grease will average between 0.50 per cent and 0.6 per cent for 35 per cent difference in relative humidity, 0.015 per cent for each per cent difference in relative humidity. A difference of 30 per cent to 40 per cent in relative humidity is not at all unusual and may occur in a laboratory within 24 hours. As a rule, however, atmospheric humidity in a room will not vary more than 20 per cent during the day if the weather conditions are fairly stable.

Electric Oven vs. Vacuum Oven. A comparison was made of drying in the electric oven at 100° C. and the vacuum oven under a vacuum of 24-25 inches at 97-98° C. Samples 1, 5, 7, 9 and 14 were used in this series. The results obtained are shown in Table VI. The average relative humidity, which fluctuated but little, was 30 per cent during the four 5-hour periods of drying.

The results indicate that the vacuum oven at this condition gives somewhat higher results on four of these samples (0.12 per cent to 0.60 per cent at the end of 20 hours drying) than the electric oven at 100° C. at each period of drying. There is practically no difference between the two methods of drying on sample

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TABLE V. EFFECT OF HUMIDITY.

Sample No.	Relative humidity %	5 Hours moisture %		10 Hours moisture %		15 Hours moisture %		20 Hours moisture %	
2	65	9.41		9.29		9 35		9.41	
		8.98	9.06	9.11	9.20	9.12	9.24	9.27	9.34
	31	9.23		9.64		9.64		9.70	
		9.43	9.33	9.82	9.73	9.86	9.75	9.92	9.81
3	65	9.88		9.98		10.06		10.10	
		9.67	9.78	9.83	9.81	9.93	10.00	9.95	10.03
	31	9.96		10.34		10.35		10.39	
		10.07	10.04	10.45	10.40	10.45	10.40	10.51	10.45
4	65	10.00		10.18		10 35		10.41	
		9.80	9.90	10.04	10. 11	10.16	10.26	10.22	10.32
	31	10.27		10.76		10.80		10.86	
		10.30	10.29	10.79	10.78	10.82	10.81	10.86	10.86
5	65	8.90		9.09		9.19		9.25	
		8.98	8.94	9.12	9.11	9.31	9.25	9.39	9.32
	31	9.32		9.78		9.83		9.93	
		9.14	9.23	9.60	9.69	9.66	9.75	9.72	9.83
6	65	8.21		8.44		8.61		8.68	
		8.34	8.28	8.56	8.50	8.74	8.68	8.81	8.75
	31	8.75		9.07		9.30		9.43	
		8.51	8.63	9.00	9.04	9.06	9.21	9.19	9.31
8	65	8.89		8.96		9.02		9.08	
		8.83	8.86	8.81	8.94	8.97	9.00	9.18	9.13
	31	9.07		9.36		9.36		9.36	
		9.22	9.15	9.51	9.44	9.51	9.44	9.52	9.44
10	65	7.14		7.27		7 36		7.47	
		7.08	7.11	7.10	7.19	7.15	7.26	7.37	7.43
	31	7.15		7.44		7.48		7.53	
		7.25	7.20	7.54	7.49	7.61	7.55	7.67	7.60
11	65	7.46		7 57		7.63		7.69	
		7.36	7.41	7.56	7.57	7.66	7.65	7.71	7.70
	31	7.82		8.21		8.21		8.23	
		7.82	7.82	8.20	8.21	8.21	8.21	8.21	8.22
12	65	6.29		6.45		6.41		6 42	
		6.38	6.33	6.47	6.46	6.52	6.46	6.49	6.46
	31	6.49		6.69		6.67		6.66	
		6.47	6.48	6.71	6.70	6.70	6.69	6.69	6.68
14	65	11.68		11.82		11.87		11.91	
		11.78	11.73	11.84	11.83	11.91	11.89	11.82	11.87
	31	12.11		12.39		12.35		12.41	
		11.88	12.00	12.09	12.24	12.29	12.32	12.29	12.36

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TABLE VI. COMPARISON OF ELECTRIC OVEN AT 100° C. AND VACUUM OVEN AT 98–99° C.
AVERAGE RELATIVE HUMIDITY, 30%.

Sample No.	Method of drying	Hours of drying							
		5 % Moisture		10 % Moisture		15 % Moisture		20 % Moisture	
1	Electric oven at 100° C.	10.48 10.48	10.48	10.35 10.34	10.36	10.54 10.58	10.56	10.58 10.61	10.60
	Vacuum oven at 97–98° C.		10.61		10.60		10.67		10.72
5	Electric oven at 100° C.	9.77 9.84	9.80	9.70 9.74	9.72	9.93 9.97	9.95	10.03 10.05	10.04
	Vacuum oven at 97–98° C.		10.06		10.10		10.23		10.30
7	Electric oven at 100° C.	9.00 9.07	9.04	9.02 9.03	9.03	9.12 9.21	9.17	9.16 9.23	9.20
	Vacuum oven at 97–98° C.		9.66		9.65		9.74		9.80
9	Electric oven at 100° C.	7.24 7.40	7.32	7.35 7.47	7.41	7.44 7.57	7.51	7.50 7.02	7.26
	Vacuum oven at 97–98° C.		7.32		7.33		7.43		7.51
14	Electric oven at 100° C.		12.82		13.07		13.03		13.02
	Vacuum oven at 97–98° C.		13.36		13.25		13.30		13.31

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9, which is a black harness leather and the only one in this experiment containing a high percentage of grease. The slight fluctuations observed between successive dryings are undoubtedly due to the fact that the relative humidity varied slightly during the drying periods.

Effect of Humidity on Analysis of Tanning Materials. It seems probable that the humidity of the atmosphere in the laboratory at the time of drying will also affect considerably the results in the analysis of tanning and indeed other organic materials. Total solids were determined in a sample of powdered chestnut wood extract by the official A. L. C. A. method, the evaporations being carried on at 35 per cent and at 65 per cent relative humidity.

TABLE VII. THE EFFECT OF HUMIDITY ON TOTAL SOLIDS OF POWDERED CHESTNUT WOOD EXTRACT.

	Total solids %
Electric oven at 100° C. (10 hrs.) relative humidity 65% —	93.25
	92.90
	93.00
	93.20
Average	93.09
Electric oven at 100° C. (10 hrs.) relative humidity 30% —	92.65
	92.60
	92.60
	92.55
Average	92.60

The results show 0.49 per cent more total solids at the higher relative humidity. This figure agrees closely with those on sole and lightly ground leather. Soluble solids and non-tannin were not determined and it cannot be said whether or not the tannin results of different analysts working under different humidity conditions or of the same analyst repeating his work, would be affected by these differences, since these soluble solids and non-tannin residues are dried together at the same time. It seems reasonable to think, however, that they would be, because the residues differ both in kind and quantity.

CONCLUSIONS.

The following conclusions drawn with reference to leather and tanning materials are probably true for other organic materials

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and the effect of relative humidity may vary much more or less with the nature of the material.

1. The loss in drying leather in 70 mm. tannin dishes is greater than is drying in 45 mm. weighing bottles. This difference increases with the time of drying and on some leathers may be greater than the limit of error even after 16 hours drying. (See Table II.)

2. Fluctuations in moisture results upon repeated drying are due largely, if not entirely, to fluctuations in the relative humidity of the atmosphere of the laboratory during the periods of drying. (See Table III.)

3. A progressive loss in weight occurs upon repeated drying of leather when the relative humidity is constant. (See Table IV.)

4. The higher the relative humidity of the laboratory at the time a determination is made, the lower the apparent moisture and the higher the total solids results will be. (See Tables V and VII.) A difference of 35 per cent in relative humidity produces a difference of ± 0.5 per cent in drying losses on ungreased leather and tanning materials, and ± 0.2 per cent on heavily greased leathers.

5. The electric oven at 100° C. gives slightly higher results than the combined evaporator and dryer. The difference is usually within the limits of working error. (See Table III.)

6. The vacuum oven at 70° C. gives lower results than the combined evaporator and dryer or electric oven at 100° C. The difference is somewhat greater than the limit of working error. (See Table III.)

7. The vacuum oven at 97-98° C. gives higher results than the electric oven at 100° C. The differences are not regular and on some samples are very considerable. (See Table VI.)

DISCUSSION.

PRESIDENT SMALL: I would like to inquire, Mr. Veitch, whether it is your idea that this progressive loss that is found, is an actual loss in moisture or whether it is due to a decomposition of some sort in the material which is being dried?

MR. VEITCH: I think, Mr. President, it is decomposition of the material that is being dried and I think (though I do not know this at all) that it is tannin or very closely related material that is being broken down very, very slowly. We got similar results

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in the work on determining grease in leather that seem to indicate something of the same thing. A chloroform extract of a material did not yield constant results on fat if tannin was present and there is a constant loss of weight. The tanning material or the chloroform extract dried separately is all right, but just as soon as they are put together there is a constant loss in weight on drying. So I think it must be the tannin itself or a closely related compound.

MR. ORTHMANN: I would like to ask Mr. Veitch as to whether the same conditions were permitted to prevail in the weighing of the samples as in the drying?

MR. VEITCH: Yes, while we worked at 65 per cent relative humidity all the work, dryings and weighings, were done in the same room at that humidity. When we were working at 30-40 per cent relative humidity we had some fluctuation, 5 per cent, I think was the maximum from day to day, the weighings and dryings were made under these conditions.

DR. BLACKADDER: Mr. Veitch, did I understand you to say that when you dried tanning extract that there was a continued loss on prolonged heating?

MR. VEITCH: No material loss. I would not say no loss because my own experience is that we have it. However, in the other case where we dried the oil and the tanning material together, the loss was very material and continued.

DR. BLACKADDER: Would you not expect from a physical-chemical consideration that the moisture in the sample at a given temperature would strike an equilibrium with the moisture in the atmosphere?

MR. VEITCH: Unquestionably that was always happening.

DR. BLACKADDER: Then, after this equilibrium was reached you would get the continued loss due to other substances like perhaps oil evaporating or tannin oxidizing. Thus you would get a curve with a break in it. Where the break in that curve came would probably be an indication of when the loss of water had ceased taken place.

MR. VEITCH: I will say that that loss occurs in these cases, but it was so small that it hardly seems worthy of any great amount of attention is successive five hours drying. Take these

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dryings at 65 per cent humidity. On one sample after 35 hours the moisture results were 9.25 per cent; 40 hours, 9.35 per cent; on another they were 10.11 per cent, 10.22 per cent; another 9.63 per cent; and 9.63 per cent; another 7.88 per cent and 7.97 per cent. The differences after longer drying are even smaller than that. Take 50 to 55 hrs. drying—9.43 per cent, 9.46 per cent; 10.38 per cent, 10.40 per cent; 9.70 per cent; 9.72 per cent; 8.06 per cent and 8.09 per cent. The decomposition as you see is very, very slow.

DR. BLACKADDER: If the percentage is as small as that, it probably would not be worth while checking it back.

MR. VEITCH: Theoretically, it is of interest, but practically I think it would not be worth while dealing with.

MR. FAUST: What variation in humidity, at the average temperature, would there be inside of that dryer?

MR. VEITCH: It will vary with the humidity of the room.

MR. FAUST: That is true, but it will not vary to any great extent, will it?

MR. VEITCH: It might readily vary 20 to 30 per cent during the time of drying, even in one day. That, of course, will be rather a rare condition, but to-day you make an analysis and the humidity let us say is 30 per cent; to-morrow you make an analysis and it might be 70 or 80 per cent in the room.

MR. FAUST: I am talking about the inside of the dryer.

MR. VEITCH: All right, the percentage will be lower, but it will be relative to the room humidity.

MR. FAUST: You have no idea just what it might be?

MR. VEITCH: If we had tables here, we could probably tell what it would be. Seventy per cent humidity in the room would be approximately 25 per cent in the dryer. It would drop something like that.

MR. FAUST: I had no idea that it would make such a difference as that.

MR. VEITCH: That is just my guess.

MR. FAUST: I did not think it would vary more than 10 degrees in the dryer.

MR. VEITCH: I think it will.

DR. BLACKADDER: In any case, if the humidity in the atmos-

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phere of the laboratory one day was 65 per cent and another day it was 35 per cent, that is two to one, would it not be twice as much one day in the drier as it was on the other day?

MR. VEITCH: We got these same fluctuations in the vacuum oven at 70° C.

DR. BLACKADDER: You would really not have a case of relative humidity in the vacuum oven. Suppose your vacuum oven were absolutely tight, you would have a saturated atmosphere in your vacuum oven.

MR. VEITCH: Not at the end.

DR. BLACKADDER: There would be nothing to wash the water vapor out of the vacuum oven.

MR. VEITCH: The moisture would undoubtedly be pulled out of the oven as well as the air.

DR. BLACKADDER: But your air has been driven out by your moisture. Your sample would dry corresponding to whatever vapor pressure was in the oven. If your vacuum pump were drawing within 7 or 8 millimeters of vacuum, then you would have as good drying as in the air. If it were only drawing within three or four centimeters of vacuum you would not have as good drying as in the air, always assuming that you have no air leaks.

MR. VEITCH: We had practically no air leaks. We pulled practically 24 to 25 inches, and we got higher results in the vacuum oven than we did in the combined dryer and evaporator and electric oven, which would tend to indicate that the vacuum oven does not retain as much moisture in the atmosphere as the combined dryer and evaporator and electric oven.

DR. BLACKADDER: I believe there must have been some air leaks.

MR. HILL: Mr. Veitch, you do not think that the variation which you got there could possibly have been due to simply the effect of the humidity during the weighing.

MR VEITCH: I do not think so, because if that were so, we would not get this conclusive and uniform data after repeated dryings on the duplicates. That it is not due to effect of humidity during weighing is also indicated by the fact that the duplicates on a sample never change their positions, throughout the whole experiment; they maintained the same relative positions, with not an exception,—that is, if bottle No. 1 is slightly heavier on the first

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weight it is to the end of the work, which to my mind eliminates such errors as you speak of, which of course we thought of and which you could reasonably expect might be present. We weighed everything out at the same sitting. Of course opening a bottle and weighing out a sample repeatedly like that is going to have some effect, and I have no doubt it did, but it has been all masked by this other much greater effect of relative humidity of the atmosphere at the time that the work was done—and that applies from the time that you start to weigh the empty bottle, until you finish weighing the dried and desiccated sample. As soon as the oven door was opened the covers were placed on the bottles, so there was but little chance for the humidity of the room to effect the results.

In weighing clean empty bottles it was found that there is very little difference in their weight at different humidities.

MR. ORTHMANN: Mr. Veitch, from your deductions would you say there was any particular advantage in using the vacuum oven?

MR. VEITCH: No, I cannot say that, Mr. Orthmann.

MR. ORTHMANN: Outside of the rapidity—it is more rapid than the other method.

MR. VEITCH: I would a good deal rather use the evaporator and dryer.

MR. ORTHMANN: If you were in a hurry, the vacuum oven would be an advantage.

MR. VEITCH: Yes.

THE MEASUREMENT OF PLUMPING BY THE CLAFLIN METHOD

1921 Committee Report

By Alan A. Claflin, Chairman

About a year ago the writer published a paper,[1] calling attention to the measurement of the volume of filtrate from liquors shaken with hide powder under standard conditions as a means of measuring the plumping value of the liquors. The Executive Committee appointed a Committee to report on this method, which for brevity is termed the Claflin Method, and asked the writer to serve as Chairman.

[1]This JOUR., 15, 234 (1921.)

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In the absence of definite suggestions from members of this committee, the writer does not feel at liberty as chairman to make any recommendations in regard to a method of his own devising, but is pleased to submit the work done by members of the committee in collated form for such consideration and action as the Association may see fit.

Due to the limited attention the chairman was able to give the subject, a relatively small amount of work was alloted, but the mass of figures produced in this small work makes it seem fortunate that more was not attempted.

Since the main question of the value of the method is that of the comparative concordance of the results, endeavor was made to keep the work in extremely simple form. The first work, therefore, was the collaborative measurement of the plumping power of solutions of lactic and acetic acids of various molar strengths.

This work was sent out in October, and is, therefore, referred to as the October work.

The directions for the work were as follows:

Make approximately molar solution of lactic and acetic acids, as follows:

90 Grams of lactic acid, in 500 cc. distilled water 20 degrees C.

30 Grams of acetic acid, in 500 cc. distilled water 20 degrees C. The lactic acid you have received. For acetic acid, use J. T. Bakers or Baker and Anderson, Glacial C. P.

Make solutions containing 2, 5, 10, 15 and 20 cc. of these molar solutions to 200 cc. of distilled water.

These solutions should be made in duplicate in standard tannin analysis bottles and it should be noted that the total volume of solution is 200 cc. and not 200 cc. of water and the acid.

To the solution in the bottles add 10 grams of 1920 hide powder and shake for ten minutes. Filter through dry cotton cloth. Preferably a previously used cloth is selected, but all cloths should be as uniform as possible.

Collect filtrate and measure volume after hide powder precipitate has ceased to drip. All dripping should cease within thirty or forty-five minutes. Use absolutely no agitation or

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pressure on hide powder once it is on the filter. It is preferable to collect the filtrate in measuring containers, *e. g.*, cc. jars, thus avoiding any loss in transference.

Report volume of filtrate to Chairman in the following form as soon as results are obtained:

2 cc. 5 cc. 10 cc. 15 cc. 20 cc.

Lactic A
Lactic B

Acetic A
Acetic B

The A and B simply represent the duplicate solutions. Kindly note the temperature of your laboratory when tests are made and have the water as near 20 degrees as possible."

The results obtained by six collaborators are herewith tabulated:

LACTIC ACID (OCTOBER WORK)

Observer	2 cc.	5 cc.	10 cc.	15 cc.	20 cc.	Blank, cc.
Marshall	98	80	64	63	55	
	98	78	64	58	55	130
Carr	104	80	67	61	64	
	98	80	68	62	60	
*Johnson	117	112	99	86	84	
	118	111	100	86	84	
Rogers	90	70	60	56	54	
	98	68	62	56	56	129
Porter	107	83	75	73	70	
	106	86	76	73	72	139
Meehan	80	66	51	49	44	
	84	62	54	43	43	
Maximum	118	112	100	86	84	
Minimum	80	62	51	43	43	
Mean	99	81	70	64	62	

*Used 1919 hide powder

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ACETIC ACID (OCTOBER WORK)

Observer	2 cc.	5 cc.	10 cc.	15 cc.	20 cc.	Blank, cc
Marshall	110	94	75	74	69	
	109	92	74	73	67	133
Carr	115	94	81	70	68	
	114	98	83	73	58	
Johnson	129	117	107	103	96	
	129	120	110	105	100	
Rogers	108	89	76	70	69	
	108	90	76	69	69	129
Porter	124	104	93	86	84	
	124	107	92	88	82	139
Meehan	95	83	68	63	53	
	95	86	73	63	56	
Maximum	129	120	110	105	100	
Minimum	95	83	68	63	53	
Mean	113	98	84	78	73	

As is the opinion of Mr. Meehan one cause of erratic results was the variable nature of the filter cloth, in April the same work was repeated except that the filtering procedure was modified as follows:

"Instead of filtering through cotton cloth as specified in directions of October 1st filter through a plug made of one half gram absorbent cotton, forced well down in throat of funnel. Use funnel sufficiently large to hold entire contents of bottle. A very satisfactory funnel size is a long stemmed type 5 inches diameter at top, and ½ inch diameter at orifice."

The results obtained by four collaborators are herewith tabulated:

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LACTIC ACID (APRIL WORK)

Observer	2 cc.	5 cc.	10 cc.	15 cc.	20 cc.	Blank cc.
Marshall	109	95	78	74	71	132
	101	94	80	74	73	
Porter	105	76	71	64	61	137
	102	78	69	61	61	
Rogers	94	75	63	59	58	132
	95	76	62	60	57	
Meehan	94	75	65	63	62	135
	95	76	65	62	61	
Maximum	109	95	80	74	73	137
Minimum	94	75	62	59	57	132
Average	99	81	69	65	63	134

ACETIC ACID (APRIL WORK)

Observer	2 cc.	5 cc.	10 cc.	15 cc.	20 cc.	Blank
Marshall	125	116	101	95	94	
	125	113	102	97	94	
Porter	128	109	97	84	76	
	135	108	94	84	79	
Rogers	115	96	85	76	71	
	116	100	81	75	71	
Meehan	114	96	86	81	73	
	114	98	86	81	74	
Maximum	135	116	102	97	94	
Minimum	114	96	81	75	71	
Average	121	104	91	84	79	

While it is to be noted that there is considerable diversity in the results obtained there is a very striking concordance in the average or mean result obtained with the lactic acid solutions, in April and October. The results with the acetic acid are not concordant, but if viewed by the curves obtained when the results are plotted considerable concordance is found.

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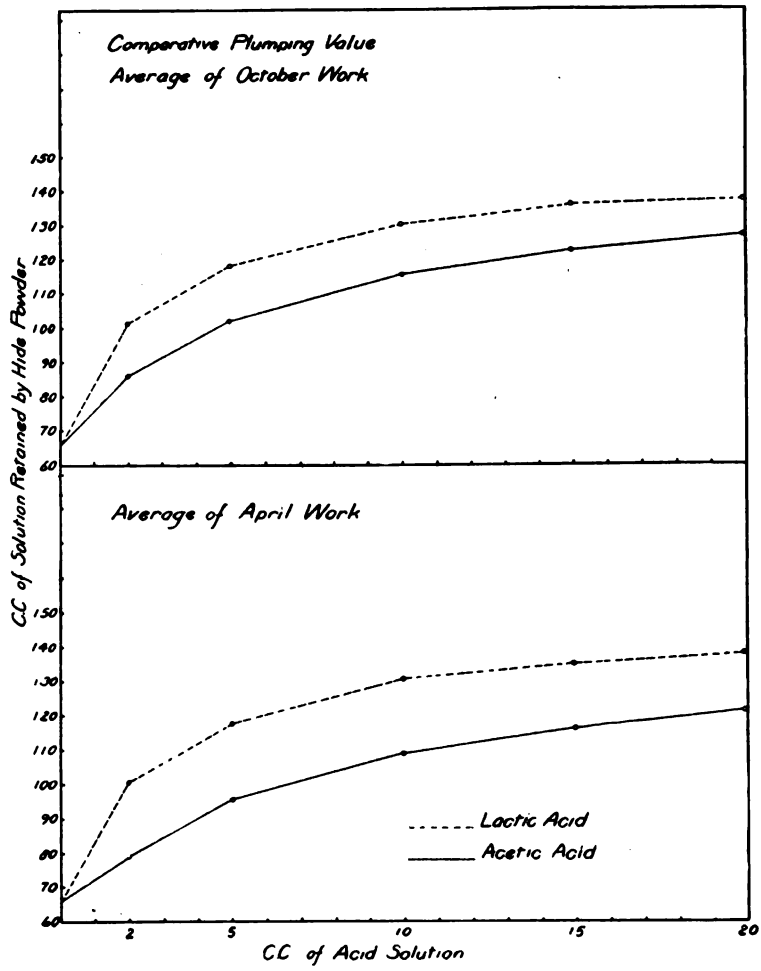

To introduce the factor of tannin into solutions containing plumping acids, a sample of Quebracho Extract was sent out with directions to use what would be approximately a ½ per cent solution of tannin with 2 cc. and 5 cc. respectively of molar lactic and acetic acids in 200 cc. of solution with the following results:

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USING ½% TANNIN SOLUTION AND MOLAR LACTIC ACID

	2 cc.	5 cc.	Blank, cc.
Porter	99	77	121
	100	78	115
Marshall	133	90	153
	128	90	148
Rogers	88	77	
	90	78	120
Meehan	102	84	123
	101	83	120
Maximum	133	90	153
Minimum	88	77	115
Mean	105	82	129

USING ½% TANNIN SOLUTION AND MOLAR ACETIC ACID

	2 cc.	5 cc.	Blank, cc
Porter	117	105	121
	119	105	115
Marshall	150	110	153
	140	112	148
Rogers	120	89	
	118	92	115
Meehan	118	104	123
	116	105	120
Maximum	150	112	153
Minimum	116	89	115
Mean	125	103	128

Since the results of Mr. Marshall show exceptional divergence from the other collaborators it is believed he used solutions containing twice as much tannin as the others. This was the fault of the chairman as the directions sent out were evidently ambiguous due to a desire to simplify the procedure.

COMMENTS BY COLLABORATORS.

J. S. Rogers.

Results by		2 cc.	20 cc.
Specified method	Lactic	90	54
		88	56
	Acetic	108	69
		108	69
Special procedure	Lactic	105	65
		109	66
	Acetic	114	73
		114	73

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It was found that when the wet hide powder was transferred from the shake bottles to the filter, that much more hide powder remained in the shake bottles when the higher concentrations of acids were used than when the lower concentrations were used, and this hide powder remaining in the shake bottle held appreciable quantities of liquid which should have appeared in the filtrate. In the special procedure the same dry non-tan cloths were used but were made into bags and the dry hide powder placed in these. The bags were then placed in the shake bottles with 200 cc. of liquid and shaken for ten minutes. The bags were then removed and placed in the funnels and the liquid poured through. This made possible the complete removal of the hide powder from the bottle and as shown above resulted in the material increase in the volume of the filtrate.

Blanks (1)—200 cc. of distilled water at 20° C. pipetted into regular shake bottle, then poured through non-tan cloth and allowed to drain 45 minutes.

(1) 191 cc.
(2) 190 cc.
Av. 190.5 cc.

(2)—200 cc. distilled water at 20 degrees C. pipetted into shake bottle, 10 grams dry hide powder added and shaken ten minutes, filtered through dry non-tan cloth and allowed to drain.

(1) 127 cc.
(2) 126 cc.
Av. 126.5 cc.

From these results it appears that the cloth and apparatus take up 9.5 cc. of water, and the dry hide powder itself takes up 64. cc. and the dry hide powder, dry cloth and apparatus take up 73.5 cc. of water. If this correction be applied to results in table No. 1 the plumping action due to the acids can be obtained.

R. E. PORTER: I believe directions for the committee work should have included the water blank tests, as the *actual plumping power* of any acid solution (or any liquor) is the difference between the water blank absorption and the absorption in such acid or liquor solutions.

I believe that the discrepancies, in the duplicate tests as shown above, is due to different swelling in the hide powder samples,

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and not due to the technique of the procedure. This opinion is arrived at through a number of preliminary tests made. Lactic acid solution was actually .89 molar. Acetic acid solution was actually .99 molar.

CHAIRMAN: In regard to special procedure recommended by Mr. Rogers while in all probability increasing accuracy, does this not complicate the method so as to make it less available for quick testing of tan liquors by assistant chemists and foremen. In regard to actual molar content as found by Mr. Porter of .89 for lactic acid, this is a discrepency that always arises due to the lactic anhydrides present.

This concludes what may be considered the strictly collaborative feature of the committee work, but there should be added thereto a paper submitted by Mr. Rile of the Barrett Company laboratories of work inaugurated by Mr. R. O. Phillips, an original member of this committee. This work was continued by Messrs. Koons and Snyder, and it seems as if it could be appropriately appended to the report of the work of the majority of the committee as a minority report.

The chairman is not at all sure that the Wilson method is not superior to his. In principle, they are similar in that they are based on the direct measurement of plumping rather than a determination of non-tanning acid, and assuming that to be a measure of plumping value. The question for the practical worker is whether the speed and ease with which the filtrate can be measured and in liquors of all colors and all gravities with a fairly constant degree of concordance does not give more truly comparative results than a method involving the uncertainties of settling. From almost any point of view the eleven days standing obviously is useless. In a warm laboratory putrefaction except as prevented by high acid content would set in, in twenty-four hours.

Another point in the Barrett report is that in regard to the 90 grams of lactic acid in 500 cc. of water being twice molar, the workers overlooked the fact that the lactic acid submitted was 50 per cent strength. Their contention would be correct if it were 100 per cent lactic acid.

The Chairman wishes to thank the members of the Committee for the work they have devoted to this subject.

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M. N. KOONS AND E. O. SNYDER: Ten grams of 1920 hide powder being shaken ten minutes in 500 cc. Erlenmeyer flasks with each of the solutions and the mixture filtered using a dry piece of cheese cloth eight inches in diameter. This cloth was placed in a four inch glass funnel similar to filter paper. The filtrates were collected in glass stoppered graduated 200 cc. cylinders.

The results are as follows the figures being cc.'s of filtrate. The difference between 200 cc. and the figures below is the volume retained by the powder.

ACETIC ACID—10 GMS. HIDE POWDER TO 200 CC.

Drained	2 cc.	5 cc.	10 cc.	15 cc.	20 cc.
15 min.	109-108	84-90	83-80-78	74-73	69-66-65
30 "	109-108	90-90	84-80-78	74-73	70-67-66
45 "	109-108	91-90	78	74-73	70-67-67

Ten grams in 200 cc. made a mush like mixture which was difficult to pour completely from the flask. In an effort to overcome this, five grams in 200 cc. was treated as above.

ACETIC ACID—5 GMS. HIDE POWDER IN 200 CC.

Drained	2 cc.	5 cc.	10 cc.	15 cc.	20 cc.
15 min.	147-146	140-138	132-130	124-123	122-122
30 "	147-146	140-138	132-131	125-126	124-123

LACTIC ACID—5 GMS. HIDE POWDER IN 200 CC.

Drained	2 cc.	5 cc.	10 cc.	15 cc.	20 cc.
15 min.	129-129	119-121	119-116	120-120	120-121
30 "	129-129	123-124	121-121	121-121	120-123

Difficulty was experienced in pouring this mixture also.

On account of the apparent superiority in greater simplicity than the above method, the method of J. A. Wilson was tried out roughly.

Two grams of hide powder were placed in 100 cc. glass stoppered graduated cylinders and filled up to the 100 cc. mark with the same solutions used in the former tests. These tests were started in the morning. During the day the cylinders were read every hour, shaken and the powder allowed to settle again for the next reading.

This shaking, settling, and reading of volume was continued for several days in an effort to observe the progress of the

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plumping. After eleven days, judging from the foul odor, active decomposition had set in and the process was stopped. The results follow, the figures indicated the apparent volume occupied by the hide powder.

ACETIC ACID

Time	2 cc.	5 cc.	10 cc.	15 cc.	20 cc
Started 9:00 A. M.	1—11—21.				
10 A. M.	46 47	51 50	55 54	55 54	56 56
11 A. M.	46 47	51 50	55 54	55 54	56 56
12 N.	46 47	51 50	56 55	56 54	57 57
1 P. M.	47 48	53 52	58 57	60 59	61 61
2 P. M.	47 48	53 52	58 58	60 59	62 62
3 P. M.	47 48	53 52	59 58	60 59	62 63
4 P. M.	47 48	53 52	59 58.5	61 60	63 63
5 P. M.	47 48	53 52	59 59	61 60	63 63
	1—12—21				
8 A. M.	48 49	54 53	60 59	62 61	64 64
12 N.	48 49	54 53	60 59	62 61	64 64
5 P. M.	48 49	54 53	60 59	62 61	64 64
	1—13—21				
8 A. M.	49 49	56 56	64 63	66 66	68 68
10 A. M.	49 51	57 57	65 64	68 67	70 70
12 N.	49 51	57 57	65 64	68 67	70 70
3 P. M.	49 51	57 57	65 64	68 67	70 70
5 P. M.	49 51	57 57	64 64	68 67	70 70
	1—14—21				
8 A. M.	49.5 51	58 57	65 65	68 67	71 71
12 N.	49.5 51	58 57.5	66.5 65	69 69	72 71
5 P. M.	49.5 51	58 58	65 63	69 69	72 71

ACETIC ACID

Time	2 cc.	5 cc.	10 cc.	15 cc.	20 cc.
	1-15-21				
8 A. M.	50 51	58 58	66 66	65 69	72 72
10 A. M.	49 51	59 59	68 67	71 71	74 73
12 N.	50 52	59 59	68 67	72 71	74 73
	1-17-21				
8 A. M.	cloudy	60 60	70 68	73 73	75 75
1 P. M.	51 52	61 61	71 69	74 74	76 76
5 P. M.	51 52	61 61	71 69	74 74	76 76
	1-18-21				
8 A. M.	51 53	61 61	71 70	75 74	77 76
12 N.	51 53	62 61	72 71	76 75	77 76
5 P. M.	51 53	62 62	72 71	76 75	77 76
	1-21-21				
8 A. M.	52 54	64 64	75 73	78 77	80 79

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LACTIC ACID

Time	2 cc.		5 cc		10 cc.		15 cc.		20 cc.	
Start 10 A. M.	2-1-21									
11 A. M.	47	45	52	52	58	57	60	59	60	61
12 N.	47	45	52	53	58	57	60	59	61	61
1 P. M.	47	46	53	53	58	57	60	59	62	63
2 P. M.	51	51	58	58	63	63	67	65	67	68
3 P. M.	50	49	57	56	63	62	66	65	66	68
4 p. M.	50	49	58	59	65	64	69	68	70	71
5 P. M.	51	50	60	60	66	66	70	69	71	72
	2-2-21									
8 A. M.	53	52	61	61	67	67	71	70	72	73
10 A. M	54	53	65	65	72	71	75	75	75	77
12 N.	53	53	64	64	71	71	76	75	76	77
1 P. M.	53	53	65	65	72	72	77	76	77	79
3 P. M.	53	52	66	66	73	73	78	77	78	79
5 P. M.	53	53	65	65	73	73	77	76	79	78
	3-3-21									
8 A. M.	57	56	67	67	74	74	77	76	78	79
12 N.	56	55	69	69	75	75	79	78	80	81
5 P. M.	57	56	70	70	76	76	79	78	79	81
	2-4-21									
9 A. M.	59	58	70	70	76	76	79	78	80	81
1 P. M.	59	58	72	72	78	78	81	81	82	84
5 P. M.	57	56	72	70	78	77	81	81	83	85
	2-5-21									
8 A. M.	60	59	73	73	80	80	84	83	83	85
12 N.	59	58	74	74	84	82	88	86	88	90

LACTIC ACID

Time	2 cc.		5 cc.		10 cc.		15 cc.		20 cc.	
	2—7—21									
8 A. M.	62	60	73	74	80	80	83	82	84	84
1 P. M.	60	60	75	74	84	81	88	90	90	92
5 P. M.	58	56	75	75	87	85	92	93	90	94
	2—8—21									
8 A. M.	62	60	75	75	82	82	85	85	86	88
1 P. M.	63	61	75	75	87	88	90	92	92	94
5 P. M.	60	59	75	76	92	87	93	94	94	96
	2—11—20									
8 A. M.	65	63	77	77	85	87	90	91	93	89

The filtration method is quick and appears to give fair checks. It is open however to error resulting from the number of variables which enter in. These include the kind of cloth used, the manner in which the cloth is supported in the funnel and the variation in the hide powder. The time and temperature variables could of course be easily standardized. The manipulation is

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difficult in that it is not possible to get all of the mixture out of the flask on to the filter cloth. This difficulty was not overcome by using less hide powder. It will be noted from the results that by this method lactic and acetic acids showed little difference.

The method of Wilson is easier to manipulate and gives better checks. It should be noted that when time and temperature are specified the only remaining variable in the method is the hide powder. The method is also apparently more sensitive, since the results obtained with lactic and acetic acids show a marked difference.

On account of the greater simplicity and greater sensitivness the method of Wilson is recommended in general idea at least. If it is looked upon with favor by the Committee, further work should be done to standardize the length of time of shaking, the time of settling, the temperatures, etc., and to determine to what extent these factors enter in. A suitable time for the test would seem to be twenty-four hours although even one hour could be used, if speed is desirable. It will be seen from the results that the greater part of the plumping takes place in twenty-four hours. The increase in volume after this point may be due to decomposition and not to real plumping.

The method of determining plumping power proposed to the Committee of the A. L. C. A. has been shown to give fair results.

Another method based on shaking the solution to be tested with hide powder, letting settle and noting the degree of settling, has been found to give better results and is recommended on account of its greater simplicity. If it is to be adopted further work must be done to standardize the conditions.

DISCUSSION.

(After the presentation of the preceding report the following discussion took place.)

PRESIDENT SMALL: As Mr. Claflin stated, this method seems rather rough and ready, and yet the surprising thing is that one is able with it to secure comparable and reasonably concordant results. As a rapid means of getting information it seems to have decided merit. Its usefulness extends beyond a mere study of the relative plumping powers of acetic and lactic acid. It is a valuable agent for numerous researches and I shall be very

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glad to hear from any of you who have made any tests with the method, or who have any suggestions to offer with regard to it.

MR. OBERFELL: Mr. Small, in working with this method I found difficulty in getting duplicates which agreed nicely and it was undoubtedly due to the amount of hide powder which stuck in the flask, or the shaking bottle, as Mr. Claflin suggested, but it was very easily overcome by returning part of the clear solution which first passed through the cloth to the shaking bottle and transferring that hide powder on to the cloth. In such a way I got very satisfactory duplicates.

PROFESSOR H. N. HOLMES: Mr. Chairman, I am very much interested in that experiment because at the present time I am writing a laboratory manual on Colloid Chemistry with a view to enabling students or men out in the industry who wish to develop something along that line to have a book that they can use in guiding them in colloid study. This experiment appeals to me as useful in such a manual as I am planning. It is worth while to demonstrate the difference in the swelling effect of the different acids on such material as hide powder, just as has been done with other protein material. That catches my fancy and I am grateful to Mr. Claflin for bringing it out now.

I think, too, of Martin Fischer's rather neat experiment on the artificial kidney. He takes, in order to show a parallel with certain kidney diseases of the body due to the development of acid in the system because of disease or other reasons, some powdered blood fibrin and puts it in a dropping funnel. He next allows acid solutions of different strength to run through it, and the fibrin swells and checks the flow of water. This pictures in the student's mind what may happen in the body when a kidney containing protein tissue, as it does, is swollen unduly by acid that may be developed in the body through faulty metabolism. Lactic acid is one of the intermediate products in the conversion of some of our food materials into carbonic acid, under certain conditions. If the kidney swells unduly and presses against its tough covering, it checks its own blood circulation. As a result, elimination of urine is greatly checked and it is impossible to wash out the toxins that have caused the trouble. Therefore, we are led to the further study of the effect of salts in repressing

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this acidic swelling of the kidney, or other parts of the body. All of this parallels what has been discussed in connection with hide powder.

DR. BALDERSTON: Mr. Claflin's method recalls the method used by Professor Procter in his article on "The Action of Dilute Acids on Gelatin," because the scheme was practically the same, namely, getting off the residual solution and then measuring it and checking results. Any one interested will find the article in our JOURNAL for June, 1911.

MR. MCLAUGHLIN: I think Mr. Claflin has made a real contribution in this work. I have been very much interested in the swelling action of acids and have worked on it considerably. There are two suggestions I would like to make. I think if he would use a hide powder of definite sized particles, which can be obtained through the use of sieves, more uniform results will be obtained. I have tried that and gotten good results.

The second point is, I wish the tannery chemists would try this method and see if they can use the findings they obtain as an index to the real plumping value of their tannery liquors. It seems to me that this method has been perfected to such a point that it should be used practically.

MR. MLEJNEK: I agree with Mr. McLaughlin that this method has been perfected to the point where it should be applied in a practical way. In working with this method we found that we could substantiate results expected from mixtures of salts and tannin in their plumping action on hide powder. We found several interesting things to be true. For instance, 5 cc. of the molar lactic acid gave the maximum plumping. Beyond that concentration no further action was observed. Also that the time factor was one which demanded some consideration. One half hour's shaking was sufficient to produce all the measurable plumping. No specific changes were noticeable after one half hour's shaking, so the bottles were allowed to stand over night after half an hour's shaking, in which case we found some additional plumping, which was not measurable by noting the changes from time to time.

It is a very good suggestion of Mr. McLaughlin's, that this method should be studied further and variables be eliminated so

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far as possible and the method should be applied to practical tannery problems.

MR. TERRASSE: One of the comments I was going to make has already been expressed. The method outlined has been in successful use for six months, daily. Unfortunately, the method has been studied only in the very simplest system of hide powder water and acid. It should be studied in the more complex systems.

MR. CLAFLIN: Mr. Chairman, there is only one thing in regard to what Dr. Balderston said about Professor Procter's work, you might say, anticipating this, I was led to this method because by experimenting, trying to repeat Procter's experiments in the crude fashion of a commercial laboratory, I never got very good results, results that would seem to be concordant, and Professor Procter, as a result of his experiments, has set forth the principle that plumping was entirely a function of the hydrogen ion. Now with this I think that a school boy or a laboratory washboy can get more concordant results than the average experienced chemist can with Professor Procter's method on gelatin. And, on the other hand, we do find that the results by this method confirm rather the work of Dr. Fischer than that of Professor Procter, in that there are other things besides the hydrogen ion concentration that affect swelling.

MR. ROBERTS: Mr. President, the thought occurred to me that possibly this might explain the reason why syntans accelerate the bark tannage, in other words, the overcoming of the astringent action of the tannic acid and plumping the skin thereby.

MR. CLAFLIN: So far as the acceleration of vegetable tannins goes, by syntans, I think that is entirely explained by the acid phase, that is, you have noted by any experiments according to this method how much more rapidly the solutions detannized in the acid phase, and so acceleration in the syntan is purely a function of the acidic character. Many acids will very much increase the absorption of the coloring matter; *e. g.*, you shake up a tanning solution that is sweet, with hide powder and the filtrate will be quite colored, but if you add a little acid of any sort and filter off you will find that a very large proportion of the color has been absorbed by the hide powder, and also that the tannin has been absorbed very much faster.

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DR. BALDERSTON: I don't like to seem to contradict, but I don't think Mr. Claflin has read Professor Procter's article carefully enough. Hundredth normal hydrochloric acid has much greater swelling action in the case of gelatin than even twentieth normal, and that does not seem to indicate that higher hydrogen ion concentration necessarily means greater swelling.

BOOK NOTICE

SOAPS AND PROTEINS. Their Colloid Chemistry in Theory and Practice. By MARTIN H. FISCHER with GEORGE D. MCLAUGHLIN and MARIAN O. HOOKER. 272 pages, 114 figures. John Wiley & Sons, Inc., New York, $4.00 net.

The author states that the studies on soaps detailed in this book were undertaken for the elucidation of purely biological questions. The soaps contain a more controllable number of purely chemical variables but their colloid-chemical behavior is much like that of the proteins. From a series of experiments with a series of pure soaps it is demonstrated that the colloid chemistry of soap-water systems call for no concepts outside those of mutual solubility and mutual emulsification or suspension. These concepts are used to explain the practices of the manufacture of soap and certain faults encountered in these operations. The analogous behavior of the "neutral" proteins and their derivatives and the fatty acids and their derivatives is established and it is demonstrated that to explain the colloid-chemistry of protein-water systems no other concepts are necessary than those established for soap-water systems. The applicability of these concepts to changes in condition of the living organism under physiological and pathological circumstances is pointed out.

The book is remarkable for its simple and clear exposition. It should be possessed and read by all leather chemists not only to add to our store of knowledge but because it treats specifically of two classes of compounds which are of primary interest to us. A knowledge of the colloid-chemical behavior and characteristics of the various soaps is essential to their intelligent use in emulsions, fat liquors, etc. While the author claims that the same mechanism explains the behavior of gelatine. For instance, the swelling of gelatine is determined by the hydration capacity of the various gelatine compounds, gelatine salts and metal gelatinates. Moreover it is extremely probable that the colloid-chemistry of soaps is identical with that of all hydrophilic colloids.

G. W. S.

ABSTRACTS

The Analytical Determination of Basicity Figures. By J. E. PICKERING. *J. S. L. T. C.*, **5**, 177 (1921). The following method was devised to overcome difficulties in observing end points in titrations for acidity. 25 grams of pure salt are dissolved in 200 cc. distilled water in a

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500 cc. beaker. 5 cc. of a 1 per cent solution of phenolphthalein are then added, and the solution neutralized if necessary. It is then brought to the boil and again neutralised if necessary. To this neutral solution, 25 cc. of the chrome liquor, which should contain between 0.15-0.25 per cent of Cr_2O_3 are added and the whole brought to a boil and then titrated with N/10 NaOH. The beaker is placed upon a white tile on the burette stand. immediately behind which is a "half-watt" lamp, covered with an opal lamp shade. The lamp should be in such a position as to allow a band of light to strike through the liquid in the breaker. Alkali is run in at a steady rate, the beaker being gently shaken at frequent intervals. As the end point is approached, the liquid seems to assume a distinct light blue colour, and the precipitated basic chromium sulphate coagulates. The addition of alkali should now proceed more slowly till the end point is indicated by a yellowish pink colour in the liquid when viewed against the lamp shade, or, by the pink colour of the solution after allowing the precipitate to settle.

It may be pointed out in connection with this determination, that the modification described by Burton and Hey, *J. S. L. T. C.*, 4, 272 (1920), will be necessary where volatile acids are present. Allowance must also be made for the presence of (i) ammonium salts, and (ii) aluminum salts.

The chromium determination is carried out as follows.

25 cc. of liquor, containing from 0.15-0.25 per cent Cr_2O_3 are diluted to about 150 cc. with distilled water, in a conical flask. Sodium peroxide is then added in small amounts at a time till the liquid assumes a light yellow colour. The solution is then boiled for thirty minutes, or longer if necessary, to decompose excess peroxide and expel dissolved oxygen. During boiling the volume of the liquid must be maintained between 15 and 150 cc. After cooling and diluting, the solution is acidified with *pure* concentrated hydrochloric acid, 25 cc. being sufficient as a rule. The liquid is cooled again and 5 cc. of a 10 per cent solution of potassium iodide are added. After allowing to stand for six to eight minutes, to ensure complete liberation of the iodine from the potassium iodide, the solution is titrated with decinormal $Na_2S_2O_3$ using starch paste as indicator.

In the case of liquors containing large amounts of organic matter and neutral salts, which render the end point uncertain. the following procedure should be adopted.

When the organic matter is merely in suspension, it is filtered through a dry filter, the first ten cc. of filtrate being rejected. If, however, the organic matter is present in a soluble form, a convenient volume of the liquor is boiled with 200 cc. of distilled water, and the chromium precipitated from the boiling solution by means of *dilute* ammonia. The precipitate is filtered from the supernatant liquor and organic matter, washed and redissolved into a conical flask with dilute hydrochloric acid, care being taken that no chromium chloride is left upon the filter. The estimation is now carried out as described above.

Attention is called to the following points, which are of vital importance in this determination:

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(a) The excess of sodium peroxide must be destroyed and any dissolved oxygen removed from the solution, for these liberate iodine from potassium iodide in acid solution.
(b) The solution must be distinctly acid to ensure the quantitative liberation of the iodine.
(c) The atmosphere should be free from nitrous fumes, as these liberate iodine from potassium iodide in acid solution.
(d) Only good quality starch should be used for the preparation of the starch paste indicator.
(e) The same amount of potassium iodide solution should be used and too large an excess avoided, as this interferes with the blue starch iodine colour.

Chrome Tanning III. The Mechanism of the Neutral Salt Effect. By D. Burton. *J. S. L. T. C.*, **5**, 183 (1921). From a consideration of the possible influences of neutral salts on each of the stages in turn into which chrome tanning was divided in a previous paper, the Neutral Salt Effect is concluded to be a function of one or more of the following factors:

I. Deceleration of Penetration by a Blockading Action of the Neutral Salt.
II. Changes in swelling due to combined effects of the acid and neutral salt present.
III. Retardation of (1) Penetration of the Chromium due to an increase in the acid taken up by the pelt with consequent production of a more basic chrome salt which would have a lower rate of diffusion; (2) Precipitation due to the increase in the acidity of the pelt which would involve a longer time for neutralisation and consequently a further retardation of tanning.

Chrome Tanning IV. The Influence of Neutral Salts on the Absorption of the Acid and Chromium from Chrome Solutions by Gelatine. By D. Burton. and A Glover. *J. S. L. T. C.*, **5**, 187 (1921).

I. Neutral salts decrease the diffusion of the chromium and the order of retardation is the same as that of the degrees of hydration.
II. Neutral chlorides cause an increase in the amount of acid taken up by the pelt, while sulphates cause a decrease in this quantity.
III. Double salt formation. as far as can be judged by a comparison of Tables I.B. and III., seem to have very little influence on the rates of diffusion.
IV. The swelling, as shown in a previous paper, may be greater in chrome solutions than in water, but the effect of adding neutral salts is to diminish this, though to an extent which renders it of minor importance in so far as the rate of tanning is concerned.

Chrome Tanning V. A Further Aspect of the Neutral Salt Effect. By D. Burton. *J. S. L. T. C.*, **5**, 192 (1921). Precipitation point determinations with violet and green chrome alum solutions and also a comparable chromium sulphate solution are described with a view to elucidating the

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cause of the rise occasioned by neutral salts. On account of several disturbing factors it was found that the only conclusion which could be drawn with certainty was that sulphates cause a greater increase than chlorides.

An explanation of the neutral salt effect is offered based on the formation of acid sulphates which correlates the facts published in this connection and suggests further work which is now in progress.

Ion Series and the Physical Properties of Proteins. III. Actions of Salts in Low Concentration. By J. Loeb. *J. Gen. Physiol.*, 1921, **3**, 391—414. The Hofmeister lyotropic series is founded on an error due to a failure to notice the influence of the added salt on P_H. At the same P_H the effect of ions on the swelling, osmotic pressure, and viscosity of gelatin depends only on the sign and valency of the ions, and univalent ions of the same sign have practically the same effect. Divalent and still more trivalent ions have a greater effect but do not differ much among themselves if they have the same sign.

Colloidal Behaviour of Proteins. By J. Loeb. *J. Gen. Physiol.*, 1921, **3**, 537—564. The potential difference between gelatine chloride solutions inside a collodion bag and an aqueous solution outside is depressed by a neutral salt in the same proportion as the osmotic pressure is depressed; the potential difference can be calculated by Nernst's formula if it is assumed to be due to the difference in the P_H measured inside and outside the bag, which latter difference seems to result from the Donnan membrane equilibrium.

Chemical and Physical Behaviour of Proteins. By J. Loeb. *Chem. and Met. Eng.*, 1921, 550. Reprinted *J. S. L. T. C.*, **5**, 146 (1921). Experiments based on the measurement of the hydrogen ion concentration have proved that the proteins combine with acids and alkalies according to the purely chemical forces of primary valency and in the same stoichmetrical relations in which acids and alkalies combine with crystalloids. They have led to the result that only the valency but not the nature of the ion in combination with a protein affects such properties as the P. D. and osmotic pressure and they have further led to the result that this fact finds its explanation in the Donnan membrane equilibrium. The classical laws of general and physical chemistry furnish us with a quantitative theory not only of the chemical behaviour of proteins but also of at least some of the physical properties.

Use of the Different Species of Acacias for Tanning. By Georges Vie, *Le Cuir*, **10**, 273-5 (1921). The usual varieties of wattle bark are briefly described. Considerable progress is being made in South Africa in the utilization of *A. decurrens* for the manufacture of extract. Profiting from the example of Natal, plantations of *A. decurrens* and *A. mollissima* have been started in British India to provide the local tanneries with extract at a reasonable price and to obtain acetic acid. acetone, methyl alcohol and other distillation products from the wood and finally to utilize possibly the spent bark for paper. An experimental plantation of 100

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hectares is situated in Southern India at 2,000 meters altitude. Another of 2,400 hectares on the plateau of Wynaad will be exempt from taxation until the first harvest, that is, five years. When the maximum normal growth has been reached the bark will be used for extract manufacture and the wood for distillation products. In planting, two or three seeds are dropped in check about two meters apart, giving about 2,500 trees per hectare. From the early experiments with wattle the yield of bark per hectare is about 28,350 kgs. and of wood, about 250 tons. Analysis of the bark gave 42.3 per cent tannin. Distillation experiments gave carbon 32 per cent; tar 9 per cent; acetic acid 5.58 per cent; and methyl alcohol 1.43 per cent. The bark of the *A. decurrens* is one of the principle exports of Natal, being normally from 12,000 to 15,000 tons per year, most of which goes to England, although Italy takes considerable. For the past year the price in France has been prohibitive.

The acacias of Algeria-Tunisia, particularly the *A. macrocarpa* and *A. eburnea,* yield pods rich in tannin. The fruit ripens in November and December. It is estimated that a plantation in hedgerows will yield 5 kgs. of fruit per running meter. The tannin bearing part of the fruit is about 50 per cent and contains 14 per cent tannin. The extraction of mimosa may be done either in open leaches or autoclaves. Theoretically the greater part of the tannin should be obtained at about 80° C. Extraction under reduced pressure is rapid and complete. Autoclaves offer still further economy in time, water and evaporation. Concentration of the extract is done as usual. Mimosa gives a reddish supple leather but is seldom used alone. A method of rapid tannage with mimosa used in Durio is described. The dry or salted hides are soaked 24 hours; then in lime, sulfide, and caustic soda for six days. After dehairing and deliming in lactic acid they are put in a 3 to 4 per cent tannin liquor for ten days and then are drummed for 48 hours in 25 per cent tannin solution. Finally the dried leather is oiled and ready for the market, giving thus a durable product of good quality.

R. W. F.

Vacuum Currying Process. ANONYMOUS. *Le Cuir* **10**, 310-12 (1921). Stuffing or currying leather by vacuum is a rather new application which is simpler than other methods of currying and gives better results. In the construction of the apparatus the principles used in the electrical industry for impregnating insulation and cables were followed. There are three important and desirable features of vacuum stuffing. The vacuum first eliminates practically all the air in the leather; the viscosity of the currying mixture is greatly reduced; and finally, as a result of having been under a vacuum, the release of the same exerts a pressure which serves to further increase the penetration of the stuffing. An examination of such treated leather will show that the penetration has been very thorough and uniform and not on the outer surfaces only as in other processes. Two photographs are given of the apparatus which was designed by an experienced currier and manufactured by the Turner

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Tanning Machinery Co. It consists essentially of a vat with automatic temperature control for melting the stuffing mixture, immediately above which is a cylindrical autoclave for containing the leather. The autoclave is equipped with a thermometer, manometer, dome door, and stopcocks for releasing the vacuum and feeding in the stuffing mixture. The latter operation is observed through two small glass peep holes in the door. The vacuum pump is connected by a system of pipes to the dome of the autoclave. The operation is very simple. The leather is rolled up, placed in a stove for about fifteen minutes and then quickly put in the autoclave. The desired vacuum is created and the stuffing mixture already heated is drawn in. After a few minutes the vacuum is released, the stuffing mixture drawn off and the leather removed to drain.

R. W. F.

Tannin Yielding Mangrove Trees of the French Colonies. By Henri Jumelle. *Le Cuir* **10**, 292-6 (1921). The term mangrove is indeed loosely applied which is regrettable since, often undesirable properities are attributed to the true mangrove through examination and analysis of samples from other trees, even at times from other families. To help overcome the present confusion considerable data are given on the mangrove and allied trees, including the scientific names, in many cases the native names, the geographic distribution, analytical data on the tannin content, and the properties of the different barks. The trees described include the *Bruguiera, Ceriops,* and *Kandelia* which are of the family *Rhizophoraceae,* the same family to which belongs the true mangrove, *Rhizophora*; the *Lumnitzera, Laguncularia,* and *Conocarpus* of the family *Combretaceae*; the *Sonneratia* of the family *Myrataceae* or according to some *Lythraceae*; the *Carapa* of the family *Meliaceae*; the *Thespesia populnea* and *Heritiera littoralis* of the family *Malvaceae*; and the *Avicennia* of the family *Verbenaceae.* Since the mangrove and associated trees are all generally tannin bearing but differ widely in their tannin content and properties it would be advisable to exhaustively study them in order that more desirable ones might be selected.

R. W. F.

Manufacture of Liquid Sodium Bisulphite. By Gabriel Desmurs. *Le Cuir* **10**, 316-8 (1921). The increasing use of sodium bisulfite makes its manufacture of interest. In a wooden vat of five cubic meters dissolve 1,000 kgs. of sodium carbonate (90 per cent Na_2CO_3) in three times its weight of tepid water and then dilute to 3,500 liters with cold water. A rich stream of dry, cool, sulfur dioxide gas is then passed into the solution until carbon dioxide is no longer set free, or until the solution is acid to phenolphthalein and neutral to methyl orange. The quantity of sulfur consumed theoretically is 548 kgs. The sulfur dioxide is provided by sulfur furnaces of two general types. One, the simpler in construction, in which the air is supplied by compression and the other, in which the air is delivered to the combustion chamber by aspiration giving better combustion. In operating the furnaces the air supply and condensation are of extreme importance. Too much air with too great a cooling of the furnace

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produce sulfur vapors which sublime in the tubes. A strong air supply with the temperature of the furnace at the highest point gives excellent combustion but a poor yield of sulfur dioxide. To keep down the formation of sulfur trioxide, which occurs normally to the extent of 2.8 per cent, the air must be absolutely dry. The maximum possible yield of sulfur dioxide is 21 per cent by volume but this is never attained in practice, the yield often being 10 per cent or less. A yield greater than 15 per cent should not be attempted as then part of the sulfur frequently sublimes.

R. W. F.

Notes on the Determination of Chrome in Chrome Liquors. By P. CHAMBARD. *Le Cuir,* **10,** 318 (1921). The sodium peroxide method, while very good for new liquors, often gives trouble with old ones. At the beginning of the oxidation with used liquors a slight flocculent precipitate is often formed which upon boiling is changed to yellow powdery calcium chromate. This does not however influence the final result as it reacts the same as the sodium chromate upon acidifying with hydrochloric acid. It happens frequently that upon adding the hydrochloric acid the solution is more or less completely reduced, changing to a green or yellowish green, and in such cases the chromium determination is low. It might be supposed at first that this reduction is due to organic matter in the old liquors but such is not the cause. If the hydrochloric acid is added drop by drop, a beautiful blue color will at first be formed, which is perchromic acid and which upon the addition of the excess of hydrochloric acid is reduced to chromic oxide and not to chromic acid. The formation of the perchromic acid may be due to peroxide compounds from the lime or calcium sulfate, which are more stable than the sodium peroxide. The difficulty can be easily avoided by prolonged boiling during the oxidation or sodium peroxide stage.

R. W. F.

Tanning Rabbit and Small Fur Skins. By GABRIEL DESMURS. *Le Cuir,* **10,** 232-33 (1921). Usually fur skins are tanned with chrome alum although a vegetable tannage of the following composition is quite successful: Ordinary quebracho extract (40 per cent tannin) 100 kg.; sumac extract (22 per cent tannin) 10 kg.; sodium sulfate (92-97 per cent Na_2SO_4) 2.5 kg.; and aluminum sulfate 0.5 kg. Rabbit skins are first softened in salt solution containing a few drops of formaldehyde. After fleshing carefully they may be tanned with the quebracho-sumac extract, 100 kg. in 2,500 liters of water sufficing for 2,000 skins. The skins must be moved frequently and are tanned in five days. The temperature should be maintained at 35° C. The skins are thoroughly and frequently stretched or worked while drying. The above formula may be used for other fur skins.

In dyeing, the tanned rabbit skins are first treated with a solution of sodium or ammonia carbonate or caustic soda. For blackening logwood or sometimes tumeric or fustic are used with copper sulfate or pyrolignite

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of iron. Wool skins are cleansed with a milk of lime, dyed black with a mixture of logwood, sumac, nut galls and pyrolignite of iron. For brown, black, and dark gray shades para-phenydiamine is used with hydrogen peroxide. Grays may be secured with sumac or pyrogallol and sulfate of iron. Browns are obtained from the para-phenylenediamine, ortho or para-amidophenol, or meta-toluylenediamine colors by oxidizing on the hair with hydrogen peroxide or potassium dichromate. Fancy shades are produced with nigrosine, Bismark brown, auramine, acid green and other aniline colors.

R. W. F.

Suggestions on Fat-Liquoring Box-Calf and Kid Leathers. ANONYMOUS. *Le Cuir,* **10**, 288-90 (1921). For successful fat-liquoring the tanned skins must be entirely freed of acids and salts by washing either in pure water or in solutions of borax, sodium bicarbonate, or potassium carbonate. Washing with water alone will not entirely remove the acid but with the use of alkalis must be carefully done. The skins should always be first washed in water as adding the alkali too soon produces an insoluble precipitate in the leather which gives difficulties in dyeing and fat-liquoring. Soft water gives the best results. The fat liquor should be suitably diluted so that it can be absorbed completely. If the oil is imperfectly emulsified, grease stains will result. A fat-liquor which contains an excess of soap, or one in which too strong a soap has been used, has a cementing action on the fibers of the leather, resulting in flat, harsh spots. It is important to warm the drum before using, and to control the temperature during fat-liquoring. Oils from neatsfoot, castor, and olive oils are recommended for glazed leathers while for dull finishes degras is preferable. Good results may be obtained in fat-liquoring chrome leather with a soap from tallow or from a mixture of tallow and olein.

The following formulas for fat-liquoring are suggested:

For calf, sheep and horse: 1.4 kgs. castor oil soap; 1.2 kgs. glycerine; and 0.8 kgs. castor oil. The addition of a little oleic acid will help to maintain the emulsion. To prepare the castor oil soap dissolve 0.45 kgs. of caustic soda in 1.5 liters of warm water and add 4.5 kgs. of castor oil heated to 35° C.

For box-calf as well as the above skins: 5 kgs. castile soap; 3 kgs. moellon; 0.5 kg. paraffine oil; 0.25 kg. sodium carbonate; 0.5 kg. casein; and 80 liters of water.

For kid: 2 kgs. neatsfoot oil; 1.5 kgs. castile soap; 1 kg. egg yolk and 0.5 kg. glycerine; or 2 per cent egg yolk; 1 per cent neatsfoot oil and 0.5 per cent castile soap.

For combination chrome and vegetable tannage: 0.5 kg. vaseline; 2 kgs. castile soap; 0.5 kg. egg yolk; and 6 kgs. castor oil.

R. W. F.

Dyeing Chrome Leather. BY HECTOR GIUSIANA. *Le Cuir,* **10**, 270-3 (1921). Uneven dyeing of chrome leather is often due to mechanical difficulties as well as to improper selection of skins and to mistakes in

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the fore-tanning, tanning and dressing processes. In drum dyeing, for example, rubbing against the walls of the drum and the folds produced make for uneven coloring. Excellent results are obtained by suspending the skins in the dye-liquor. A sketch and a description are given of a vat for this purpose, in which the dye liquor is kept in rapid motion by means of a pump. The skins are suspended over brass rods fitted with rubber jackets having four lengthwise ridges so that the skins touch the rods only at these points. During dyeing the rods are turned a little at intervals to avoid pole marks. A coil is also provided for heating the liquor since in other than vegetable dyeing the best results are obtained by gradually raising the temperature as is done in textile dyeing. For example the dyeing may be started at 40° C. and raised to 65° to 70° C. in half an hour and maintained there until the dyeing is completed. This is a great advantage over drum dyeing where the temperature gradually falls during the operation.

R. W. F.

The Manufacture of Artificial Leather. By M. de Keghel. *Le Cuir*, **10**, 184 and 250 (1921). While there are almost innumerable processes for the manufacture of artificial leather they are all based primarily upon processes similar to the manufacture of oil cloth or linoleum. The first consists of an animal or vegetable fabric as a base with several layers of a suitable paste which is then pressed and calendered; the second of mixtures of very finely divided substances with certain adhesive which are subjected to very high pressures. A large number of processes are described somewhat in detail giving the principle ingredients for each one. Among the various materials mentioned are leather, paper, mill-board, hay, straw, and wood-pulp wastes; caoutchouc, resins, linseed oil, drying, oil, varnishes, nitro-cellulose cellulose acetate, tars, pitch, silicates, iron filings, sand, cork, albumen, casein, gelatine, tannic acid.

R. W. F.

Tanning Action and the Swelling of Unhaired Skins. By Georg Grasser, *Collegium* **609**, 1-10; **610**; 58-67; **611**, 105 (1921). "Previous work had shown that unhaired skin was a suitable material for use in studying the swelling action of acids so it was also used in the study of the swelling caused by tannins and by acids in the presence of tannin. Two gram pieces of skin in a total volume of 20 cc. were used in all cases. Varying amounts of tannin with 2 cc. N hydrochloric acid were first used, but the tannin had no effect on the swelling. With 2 cc. N hydrochloric acid and 4 cc. of 10 per cent tannin solution in 14 cc. of water a maximum swelling was reached in 90 minutes, but the decrease after 90 minutes was slight. The influence of tannin on the swelling was also negligible when less than 2 cc. of acid was present, for with 4 cc. of a 10 per cent tannin solution and increasing amounts of acid (up to 0.7 cc.) in a total volume of 20 cc. the swelling was proportional to the amount of acid present. Tannin alone had no swelling action. It caused a slight increase in weight which became constant ($q = 0.39$) after eight hours, probably due to the fact that there was a decrease in water content equal to increase in tannin

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adsorption. The original tannin solution was slightly acid but it soon became slightly alkaline. This could have been caused by a trace of gallic acid which was rapidly absorbed. If the gallic acid had caused a slight swelling this should have been decreased by salt or sodium hydroxide but increasing amounts of each either had no effect or caused a slight increase in the weight of the skin. Salt alone caused a slight increase in the weight of the skin. Pieces of skin were next treated for six hours with 2 cc. N hydrochloric acid and increasing amounts of formaldehyde. The swelling due to the acid and the amount of acid absorbed were both decreased greatly by the formaldehyde and when the skin was treated with formaldehyde alone it was depleted. Swelling by sodium hydroxide was almost entirely repressed by formaldehyde or if much formaldehyde was present, there was a depleting action. The author concludes "that formaldehyde has an extraordinary depleting action and that this is retained even in the presence of acids or alkalies," and that in this "formaldehyde is an exception to all tested adstringents and tannins." Phenol did not influence the swelling caused by acids but decreased greatly the swelling caused by alkalies. Although tannin has no influence on the swelling when the acid and tannin act simultaneously, this is not true if the tannin is allowed to act first. To investigate this action the following procedure was used: m(=2) gram pieces of skin were first treated sixteen hours with the tannin solution, and then for six hours with a dilute hydrochloric acid solution (2 cc. N hydrochloric in 20 cc. water). The velocity of swelling, K_1 is given by the formula. $K_1=\frac{\text{Log } (m+a)/m.}{0.4343\sqrt{6}}$

"a" is the increase in weight of the piece of skin due to the acid swelling. The velocity of swelling of a piece of skin treated for six hours in acid alone is given by the formula. $K_2=\frac{\text{Log } (m+q)/m.}{0.4343\sqrt{6}}$

Then $K_2=K_1$ f. and approximately $f=\frac{m+q}{m+a}$.

The velocity of tanning, C, is calculated from the formula $C=f/q$. The value of C for pure water varied from 0.33 to 0.38. If the value of C for any material is greater than the value of C for water the material has a true tanning action but if the value is near that for water, the material has only a pickling action. The inert substances, salt and sugar, had no influence on acid swelling. Tannin from galls tanned moderately rapidly, C = .44, in moderately concentrated solutions, while C rose to 0.54 in very concentrated solutions. For dilute chestnut wood extract of ordinary tanning strength the velocity C was 0.41 while in stronger solutions it was 0.48. Quebracho wood extract, oak bark extract, pine bark extract and valonea all tanned at about the same rate, C varying from 0.38 to 0.42 for 2° Bé solutions. Sumac and catechu were both good tanning materials, the value of C being 0.45 for solutions containing 2 grams of extract in 20 cc. of solution. Mangrove and logwood

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in solutions of 2° Bé had very little tanning action, the value of C being only 0.35. Sulfite cellulose tanned rapidly but this will be shown to be due to the salt content. Neradol D and ND and Ordoval G all tanned very rapidly and this was not due to the salt content since Neradol ND which has the lowest ash tanned most rapidly. Neradol ND has a greater velocity of tanning than any other practical tannin, the value of C being 0.95 for a 2° Bé solution. Picric acid and phenol were good tannins but hydrochinon, pyrogallol, resorcin and pyrocatechin were not tannins according to this test. Basic chrome alum solution containing 20 grams of chrome alum and 5.5 grams of soda in 200 cc. had a tanning action almost equal to that of the synthetic tannins. The average for C from several tests was 0.72. Basic iron chloride, zinc sulfate and potash alum without salt had no tanning action. Turkey red oil had a very slight tanning action for C had the value 0.42 in a 10 per cent solution. Formaldehyde, by this test, was one of the best tanning substances. The value of C varied from 0.84 to 0.93 as the concentration of the solution varied from 2 to 16 cc. of formaldehyde in a total volume of 20 cc. Formaldehyde decreases the swelling by acids when it acts on the skin before or at the same time as the acid, but it had no depleting action when the skin was first swollen in acid and then immersed in the formaldehyde. The intensity of the tanning was next investigated by allowing the tannin to act for various times and determining the maximum ability of the tannin to prevent swelling by acid. In this work 2 gram pieces of skin were placed in five 50 cc. portions of 1° Bé solution of the substance to be tested. The skins were removed from the five portions at the end of 16, 40, 64, 88 and 112 hours resp. and then placed in 20 cc. of water containing 2 cc. N hydrochloric acid. After six hours they were removed and weighed.

The following table gives the results for some of the materials investigated. C is the velocity of tanning, J is the tanning intensity or the maximum velocity, t is the time required to reach the maximum value for J, and E is the final tanning velocity or J/t.

Tannin	C	J	T	E
Chestnut	0.48	0.48	88	0.54
Quebracho	0.46	0.58	112	0.51
Mangrove	0.42	0.41	112	0.36
Logwood	0.36	0.43	112	0.38
Tannin	0.49	0.73	112	0.65
Neradol D	0.76	0.89	112	0.79
Neradol ND	0.95	0.96	16	5.62
Formaldehyde	0.93	0.97	40	2.42
Sulfite cellulose ext.	0.50	0.40	112	0.35
Phenol	0.62	(9.63)	—	(3.87)
Basic chromium sulfate	0.78	0.78	16	4.87
Basic iron chloride	0.39	0.36	112	0.32
Potash alum	0.40	0.36	112	0.32
Water	0.36	0.36	—	—

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The ability to precipitate gelatin and a large value for E is not characteristic of tannins alone as is shown in the case of phenol. True tannins need not give maximum values for C, J and E. For the tannins investigated the average value for J was 0.45-0.58, for C 0.40-0.49, and for E 0.40-0.54.

I. D. C.

Aldehyde Tannage VIII. By W. Moeller, *Coll.*, **613**, 217-20 (1921). Previous work has shown that hide powder is capable of adsorbing much greater quantities of formaldehyde than is adsorbed in practice, and that formaldehyde is the slowest of all tannins. To show that the adsorption was dependent on the time, an extremely finely divided hide powder was treated for one month with 30 per cent formaldehyde, then removed, air dried for several days and a portion dried at 100° C. Analysis of the solution showed that 178.3 per cent of formaldehyde, calculated on the weight of hide powder, had been adsorbed. Nitrogen determinations on the tanned powder, however, showed an adsorption of only 7.82 per cent Only 7 per cent is therefore adsorbed in the polymerized form and the remainder is probably adsorbed in a gaseous form similar to the adsorption of gases by charcoal. However the dry hide powder was added to the formaldehyde solution and there was thus no opportunity for solution of interfibrillary material and the setting up of a peptised tanning system. The experiment will be repeated first soaking the hide powder in distilled water. While pelt usually adsorbs only 3 per cent or 4 per cent of formaldehyde, a piece left in a 15 per cent solution for two months adsorbs 20.36 per cent and a greater adsorption is expected in the experiment which is still in progress where a longer time will be given for the adsorption. Since the adsorption depends on the time, tanning with formaldehyde can not be a true chemical but must be a colloidal-chemical process.

I. D. C.

The Determination of Sugar-like Materials in Leather By C. van der Hoeven, *Coll.*, **613**, 220-4 (1921). On account of the length of time required for the gravimetric determination the following method, a modification of that of Schoorl (Zeit. für A. Chem. 1899 p. 633), was worked out. The usual procedure was followed up to the reduction; that is the extract was clarified with basic lead acetate, the excess lead removed with sodium corbonate, and the solution then inverted by heating with dilute sulfuric acid in a water bath at 100° C. for 30 minutes. An aliquot of this and water was added to 20 cc. of Fehlings solution of Soxhlet-Meissl-Herzfeld so that the total volume was 50 cc. This was heated to boiling in 3 minutes and boiled for 2 minutes and then cooled quickly in water not below 25° C. Three grams of potassium iodide dissolved in water and 10 cc. of 25 per cent sulfuric acid was added and the iodine titrated with 0.1 N sodium thiosulfate. Tests showed that this method agreed well with the gravimetric method. However it was better to use

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a larger volume for reduction so that the total volume was 100 or 150 cc. instead of 50 cc. It was then necessary to boil for 4 or 8 minutes resp. instead of 2 minutes.

I. D. C.

Notes on Moeller's Work, "The Relation Between Hydrolysis and Adsorption." By V. Kubelka. *Coll.*, **611**, 135-41 (1921). Previous work on the adsorption of acids by skins is considered valueless by Moeller (*Coll.*, 1920, p. 109) because the workers allowed only a short time for equilibrium to be reached and did not consider the factors which enter in a longer period of time, and also because they did not consider the effect of the dissolved hide substance. "Secondary" changes, however, take place in all adsorptions but they are too slow to affect the equilibrium. Although Moeller states that the adsorption of hydrochloric acid is a case of true adsorption, this "adsorption" does not depend on the concentration of the solution at equilibrium but is independent of both concentration and time. Kubelka offers the following criticisms of the work of Moeller. The determination of the hydrolysed hide substance is the only new thing introduced. The accuracy of the analytical methods was not investigated and the limits of error are not given. Determinations at a sufficient number of concentrations and times were not made. Calculation of the minimum possible error shows that it is as great or greater than the results. Dissolved carbon dioxide in the solutions would cause an error equal to the results and since the carbon dioxide content varies witn external conditions the results are not comparable.

I. D. C.

Tanning Materials in the Years 1914 to 1918. By M. Smaic and J. Wladika. *Collegium*, **609**, 34-44; **610**, 88-92; **611**, 142; **612**, 193; **613**, 236 (1921).

Pine bark was one of the principal substitute tanning materials used after imports of tanning materials ceased. The average of a large number of analyses of bark from various parts of the country was as follows;—Moisture 15 per cent, tannins 12 per cent and non-tannins 10 per cent. Pine bark extract was increasingly used during the war, and the average analysis of a 23° Bé extract at 17° C. was, tannin 21.3 per cent, non-tannin 21.1 per cent, moisture 56.8 per cent, and ash 2.3 per cent. Bruml-Silberberger developed a process in which the rosin was extracted from the bark with benzine before extracting the tannin. This gave an extract containing 21.8 per cent, tannin and 20.8 per cent non-tannin, and which was a more satisfactory tanning material especially in the suspending vats. The shortage of casks in some parts of the country led to the production of very thick or even solid extracts. The thick extract contained on the average 25.5 per cent tan and 26.7 per cent nontannin while the average analysis of the solid extract was tannin 44.7 per cent, nontannin 38.0 per cent, moisture 16.2 per cent, and ash 1.9 per cent. Pine twigs were used only locally since they were difficult to gather and transport and since the ratio of tannin to non-tannin was very low. Pine

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wood extract was really sulfite-cellulose extract and was usually mixed with other tanning materials. Sulfite-cellulose extract is taken up by the hide and aids the absorption of tannins but since it has no true tanning action, its use was forbidden by the military authorities. The average analysis of sulfite-cellulose extract follows:

	Liquid (25.7 Bé) Per cent	Solid Per cent
Adsorbed by hide,	21.9	46.7
Not adsorbed by hide,	25.6	40.0
Moisture,	52.1	13.3
Ash,	7.3	12.8

Fir bark is a good tanning material, although it has considerable swelling action and contains only about 5 per cent tan. Larch bark contains 8 per cent tannin but is not very abundant, so that fir and larch barks were used only locally.

Analyses are given of various samples of the following tanning materials collected during 1914-8: oak bark and wood, chestnut bark and wood, valonea, trillo, knoppern, sumac, and extracts of these materials. These differ little from the pre-war values. Extracts were made when possible on account of the difficulty and cost of transporting the raw material. The small tanneries also made use of hops, hop stems, beech bark and nuts, and the barks of the alder, willow, walnut and birch. They are all poor in tannin and are useful only when mixed with other materials, so that transportation to the larger tanneries would be too expensive. Willow bark does not give weight but is valuable for tanning light leather.

I. D. C.

PATENTS

Coloring-Matter for Leather and Method of Using the Same. U. S. Patent 1,371,572. J. H. PFINGSTEN, Milwaukee, Wis. Filed July 2, 1917. A process of coloring leather which consists in suspending pulverulent, insoluble pigment in water and agitating the leather therein in the presence of heat so that the pigment is uniformly deposited in the interstices of the leather.

Leather-Working Machine. U. S. Patent 1,375,935. C. A. SAWYER, JR., Newton, Mass. Filed May 8, 1920.

Method of and Apparatus for Treating Leather. U. S. Patent 1,376,238. C. L. WHITNEY, Conneaut, Ohio, Filed May 1, 1920. The method of treating hides and skins which consists in setting out a hide on a drum and mechanically rotating the latter, and then transferring the hide from the drum directly to a movable drying frame, such transference being effected by the relative movement of said drum and frame without manually handling the hide.

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Process of Producing a Surrogate for Tannin. U. S. Patent 1,376,805. CARL GRAF, Cologne-Rodenkirchen, Germany, assignor, by mesne assignments, to The Chemical Foundation, Inc. Filed March 11, 1916. That process of producing a surrogate for tannin, which comprises treating tar with an aqueous solution of an alkali or its equivalent; separating the liquid thus obtained; and treating said liquid with sulfate of copper and sulfate of aluminum.

Method of Coloring and Finishing the Surface of Grain-Leather. U. S. Patent 1,376,961. W. H. MEADE AND S. H. FRIESTEDT, Camden, N. J. Filed July 24, 1919. As a new article of manufacture, leather having a surface coated by metal precipitated from a soluble compound.

Leather-Making Process. U. S. Patent 1,378,213. P. BRANDT, Bristol, Ind., and H. T. WILSON, Petoskey, Mich. Filed July 31, 1918. That part of the process of making leather which comprises subjecting the partly prepared leather containing tannin to the action of dissolved gluey matter and tannin in the presence of an alkaline material. and thereafter to an acid solution.

Leather-Working Machine. U. S. Patent 1,382,584. C. A. WILLIAMS, Torquay, England, assignor to Clark, Son & Morland, Ltd., Glastonbury, England. Filed Sept. 24, 1918.

Scouring and Leather-Dressing Compositions. British Patent 160,738. A. T. HOUGH, Choisy-le-Roi, Seine, France. July 30, 1920. A composition to be mixed with water to scour leather, with soda solution to scour wool, and with oils to dress leather, is prepared by mixing a neutralized sulphonated oil such as sulphoricinate of soda or ammonia with an organic solvent, preferably non-inflammable. Solvents specified are carbon tetrachloride, tetrachlorethane, tetrahydronaphthalene, benzene. and naptha.

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CORRECTION

In the article, the Determination of Available Calcium Oxide in Lime used for Unhairing Hides, on page 439, lines 8 and 21, "calium" should be "calcium." Page 440, line 26, "Schaife" should be "Scaife." Page 441, line 3 omit the period after "shake." Table I as given below should supplant Table I as given on page 442.

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TABLE I. EFFECT OF FINENESS AND AGITATION ON DETERMINATION OF AVAILABLE LIME BY METHOD I.

Sample No. 1. Method of Shaking	20 Mesh	40 Mesh	60 Mesh	80 Mesh	100 Mesh
			Per cent available CaO.		
Shaken 5 min	39.3	41.8	51.9	54.4	57.2
Shaken 10 min	46.0	46.3		58.1	60.0
Shaken 5 min. stood 3 hrs., shaken 5 min.		51.9	57.5	60.9	63.7
Shaken 10 min. stood 3 hrs., shaken 10 min.		57.8	64.5	64.8	65.1
Shaken 5 min. stood 3 hrs., shaken 5 min. stood over night, shaken 5 min.		60.0	65.1	65.2	65.3
Shaken 5 min. stood 3 hrs., shaken 5 min. stood over night, shaken 5 min., stood 3 hrs., shaken 5 min.		60.6	65.1	65.1	65.3
Shaken 10 min. stood 3 hrs., shaken 10 min. stood over night, shaken 10 min., stood 3 hrs. shaken 10 min.		64.5	65.2	65.1	65.3
Shaken 6 – 2 min. periods, at 1 hr. intervals.			62.8		
Shaken 6 – 5 min. periods, at 1 hr. intervals.			65.3		
Shaken 6 – 2 min. periods, at 1 hr. intervals. stood over night, shaken 2 min.			64.5		
Shaken 6 – 5 min. periods, at 1 hr. intervals, stood overnight, shaken 5 min.			65.3		
Shaken in rotary shaker for five hours (10 revolutions per min.)			65.3		

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DETERMINATION OF EPSOM SALTS IN LEATHER*

1921 Committee Report

By R. W. Frey, Chairman

The committee assignment for this year was primarily to make a direct comparison of the gravimetric and volumetric determination of magnesium in leather. It was also suggested that it might be desirable to propose an official method.

A brief review of the literature will show that a great deal of work has been done on the determination of magnesium and that there has been considerable difference of opinions as to the proper conditions for the accurate determination of magnesium when precipitated as the ammonium phosphate compound. Neubauer[1] has found that precipitation is complete even in the presence of large quantities of ammonium salts but that by the usual practice of precipitation in the cold sometimes high and at other times low results are obtained. The former is so when precipitation occurs in slightly ammoniacal or neutral solutions containing large quantities of ammonium salts. Low results are obtained when the precipitation is made in strongly ammoniacal solutions with but little ammonium salts and particularly with the slow addition of the phosphate solution. Neubauer recommends a double cold precipitation, adding the phosphate solution to the slightly acid magnesium solution and avoiding excess of ammonium salts and of precipitant in the second precipitation. Gooch and Austin[2] also agree that the best working conditions are the absence of large excess of precipitant, ammonium salts, and ammonia. They show that large amounts of ammonia are not only unnecessary but harmful until, at least, the precipitate has practically all formed. They also propose the addition of the precipitant to the slightly acid solution, followed by ammonia in excess. It has thus developed from this and other work that the best conditions require either removal of ammonium salts before precipitation, or double precipitation, avoiding in the second one excessive quantities of ammonium salts and of precipitant.

*Read at the 18th Annual Meeting at Atlantic City, June 11, 1921.

[1] *Z. Angew. Chem.*, 1896, 439.

[2] *Am. Jour. Sci.*, 4, 7, 1899, 187.

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More recently there has been a somewhat general tendency to propose hot precipitation when only one precipitation is made, the claim being that reasonably accurate results are thus obtained in the presence of excess of precipitant and of ammonium salts. Gooch and Austin in their work called attention to a method of hot precipitation proposed long ago by W. Gibbs.[3] The new editions of recognized standard books are also quite in accord on this and propose either the method of W. Gibbs or B. Schmitz.[4] These methods for precipitation are essentially as follows: Heat the neutral or slightly acid solution to boiling, add drop by drop an excess of sodium or ammonium phosphate solution and then one-third of the solution's volume of 10 per cent ammonia. The solution is then allowed to stand and cool and is proceeded with as usual.

In view of all this it was thought that a study of conditions for precipitation of magnesium would be of as much or more value than a comparison of the gravimetric and volumetric procedures, and consequently an effort was made to include some work in cold and hot single precipitation of magnesium as phosphate under conditions about like those met with in leather analysis. Only single precipitation was considered for the present. It may develop that double precipitation will be necessary but because of the time the same would require it should not be considered until the need for it in leather analysis has been shown.

It was the intention of the chairman to secure or prepare as a starting point a material of accurately known magnesium content, with the magnesium content preferably determined by some method other than the ammonium magnesium phosphate precipitation. Pressure of other work however made this impossible and in order to accomplish at least the principal assignment of a direct comparison of the gravimetric and volumetric procedures, the best that could be done in the time available was to use a samples of so-called pure MgO. For the entire committee a stock solution was made by the chairman by dissolving an accurately weighed quantity of MgO in the smallest quantity of pure H_2SO_4 required for solution. A portion of this stock

[3] *Am. Jour. Sci.*, 3, 5, 1873, 114.
[4] *Zeitschr. Anal. Chemie.*, 44, 1905, 335.

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solution was sent to each member who in turn diluted an accurately measured 100 cc. aliquot to one liter with distilled water at 20° C. for his "Solution No. 1." Before making up this stock solution the sample MgO was analyzed for magnesium and the average of nine good agreeing determinations by cold precipitation as ammonium magnesium phosphate, including both the recognized double precipitation and single precipitation avoiding excessive quantities of ammonium salts, gave 96.2 per cent MgO. After ignition of the MgO a residue of 96.8 per cent was obtained and qualitative examination showed traces of small amounts of barium, calcium, chlorides and sulphates. The two figures, 96.2 per cent and 96.8 per cent, are in pretty good agreement. Now for "Solution No. 1" the MgO was accurately weighed out on the basis of 0.000818 gms. of sample per cc. of "Solution No. 1." Taking the value 96.2 per cent MgO and the factor 6.1133 for conversion of MgO to $MgSO_4 7H_2O$ gives 1 cc. of "Solution No. 1" equivalent to 0.00481 gms. $MgSO_4 7H_2O$; 5 cc. to 0.02405 gms.; and 25 cc. to 0.12025 gms. These then may also be taken as theoretical values for "Solution No. 1," in addition to the standardization values obtained by each member of the committee.

The committee consisted of C. A. Blair, L. A. Cuthbert, F. F. Marshall, A. C. Orthmann, J. S. Rogers, and R. W. Frey. Mr. Blair and Mr. Rogers were not able to report. Several members of the committee kindly furnished samples of leather as follows:

Leather No. 1—Oak leather, no added epsom salts.
" No. 2—Union leather, no added epsom salts.
" No. 3—Hemlock leather, with added epsom salts.
" No. 4—Union leather, with added epsom salts.
" No. 5—Union leather, with added epsom salts.

The following directions were sent out to each member to cover standardization of the magnesium sulphate solution; comparison of cold and hot precipitation of ammonium magnesium phosphate in presence of relatively large quantities of ammonium salts; comparison of different methods for removal of ammonia wash water in the volumetric method; and direct comparison of the gravimetric and volumetric methods using leathers with and without added magnesium sulphate.

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Directions.

This year's assignment for the Epsom Salts Committee is primarily a comparative study of the gravimetric and volumetric determination of epsom salts in leather with the object, it is assumed, of recommending either a gravimetric or volumetric method, or possibly both, for incorporation in the official method. It has been gathered from conversation and correspondence that the members of the A. L. C. A. are quite divided in their opinions and it would seem particularly desirable to settle now the relative merits of these two procedures.

While the directions from the council were not specific, it has been thought best to confine the work, for the present at least, to the development of a satisfactory method or methods for vegetable tanned heavy leathers, since the epsom salts determination is desired primarily for this class of leathers and since the special tannages such as combination tannages, pyrophosphate tannage, iron tannage and so on, would require possibly numerous modifications to fit the particular type.

Those unfamiliar with the volumetric determination of magnesium should refer if possible to the Journal of the American Chemical Society, Vol. 22, page 31, in which the results of a study on the subject by James Otis Handy are given.

Section I. Preparation and Standardization of Stock Solution of Epsom Salts.

The solution labeled "For Making up Stock Solution of Epsom Salts" is an aliquot of a solution prepared by the chairman by dissolving Kahlbaum's MgO in a very slight excess of pure H_2SO_4.

Cool the solution labeled "For Making up Stock Solution of Epsom Salts" to 20° C.; pipette exactly 100 cc. into a one liter volumetric flask; fill to the mark with distilled water at 20° C.; mix thoroughly and label as follows:

"Solution No. 1: Stock Solution of Epsom Salts,

Measure all aliquots of this solution at 20° C."

This solution will be referred to hereafter simply as "Solution No. 1."

To standardize this solution, measure from a burette two 25 cc. aliquots and treat each as follows: (a) Add 2–3 cc. conc.

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HCl, just neutralize with NH_4OH (do not go way over), acidify with one or two drops of conc. HCl, dilute to about 75 cc. with H_2O and cool to room temperature if necessary. (b) Add an excess, about 10 cc., of a saturated solution of sodium ammonium hydrogen phosphate. (If a slight precipitate forms here, clear up with a drop or two of HCl.)

While stirring add a few drops of NH_4OH, just until precipitation starts; stir for about a minute; let stand 15 minutes; then while stirring slowly, add 10 cc. conc. NH_4OH (sp. gr. 0.90); cover the beaker and allow to stand at room temperature over night. (c) Filter through a well prepared weighed Gooch crucible, wash the precipitate free from chlorides with dilute ammonia water (1 part conc. NH_4OH sp. gr. 0.90 to 9 parts H_2O) and finally just moisten the precipitate with a few drops of a solution of approximately 50 per cent NH_4NO_3 in dilute ammonia water (1 part conc. NH_4OH sp. gr. 0.90 to 9 parts H_2O). Dry the precipitate, ignite gently at first, then cover the crucible and ignite intensely over a Bunsen or Meker for 15–20 minute intervals until constant in weight. Weigh as $Mg_2P_2O_7$, multiply by 2.2135 to convert to $MgSO_4 7H_2O$ and calculate the value of 1 cc. of "Solution No. 1" in terms of grams $MgSO_4 7H_2O$. Repeat the above work on another date and record all results in Table I. Take the average of all results as the standardization value for 1 cc. of "Solution No. 1" in grams $MgSO_4 7H_2O$.

SECTION II. COMPARISON OF COLD AND HOT PRECIPITATION OF AMMONIUM MAGNESIUM PHOSPHATE IN PRESENCE OF RELATIVELY LARGE QUANTITIES OF AMMONIUM SALTS.

Before proceeding to the direct comparison of the gravimetric and volumetric methods it would seem advisable, in view of comparatively recent work, to first study the best conditions for the *single* precipitation of magnesium in the presence of about such quantities of ammonium and magnesium salts as are likely to be found in the average leather ash solution.

Measure from a burette four 5 cc. aliquots of "Solution No. 1;" dilute each to about 25 cc. with H_2O, add to each 5 cc. of conc. HCl and one or two drops of conc. HNO_3; just neutralize with NH_4OH; acidify with one or two drops of conc. HCl; add 5 cc.

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of a saturated ammonium oxalate solution; dilute each to about 75 cc. with H_2O and cool to room temperature. Proceed with two of the aliquots exactly as described in (b) and (c), Section I, using, however, 5 cc. of saturated sodium ammonium hydrogen phosphate solution instead of 10 cc.

With the other two aliquots proceed as follows: (d) Bring just to boiling temperature, add to each 5 cc. of saturated sodium ammonium hydrogen phosphate solution (If a slight precipitate forms here, clear up with a drop or two of HCl), stir well and gently boil for 2 or 3 minutes. While stirring add 10–12 cc. conc. NH_4OH slowly and cautiously to prevent loss from spattering. Remove from the flame, cover the beaker and allow to stand at room temperature over night. From here proceed exactly as directed under (c) Section I.

Repeat all of Section II, using four 25 cc. aliquots of "Solution No. 1;" add to each aliquot 10 cc. of conc. HCl, and one or two drops of conc. HNO_3; just neutralize with NH_4OH; acidify with one or two drops of conc. HCl; add 10 cc. of saturated ammonium oxalate solution; dilute each aliquot to about 75 cc. with H_2O and cool to room temperature. Proceed with two of the aliquots exactly as described in (b) and (c) of Section I, using an excess, about 10 cc. of saturated sodium ammonium hydrogen phosphate solution.

With the other two aliquots, proceed exactly as directed for (d) Section II, using an excess, about 10 cc., of saturated sodium ammonium hydrogen phosphate solution.

Calculate results to grams $MgSO_4 7H_2O$ for each aliquot, and record all results in Table II, together with the theoretical quantity of $MgSO_4 7H_2O$ present in 5 cc. and 25 cc. aliquots respectively of "Solution No. 1," as determined from your standardization value in Section I.

From a comparison of the results by cold and hot precipitation of ammonium magnesium phosphate with the theoretical value select the procedure of precipitation which gives the better results, or if both give equally good results choose the one which you prefer and use it in all subsequent precipitations of magnesium. State your choice in Table II.

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SECTION III. COMPARISON OF DIFFERENT METHODS FOR REMOVAL OF AMMONIA WASH WATER IN VOLUMETRIC METHOD.

Measure from a burette six 25 cc. aliquots of "Solution No. 1," add to each aliquot 5 cc. of conc. HCl; just neutralize with NH_4OH; acidify with 1–2 drops of conc. HCl; dilute each aliquot to about 75 cc. with H_2O and cool to room temperature if necessary. Precipitate the magnesium with 10 cc. of a saturated solution of sodium ammonium hydrogen phosphate using, according to your findings in Section II, either the cold precipitation as directed under (b) Section I or the hot precipitation as directed under (d) Section II.

After precipitation over-night, filter each aliquot through quantitative filter paper; wash the precipitate free from chlorides with ammonia water (1 part conc. NH_4OH sp. gr. 0.90 to 9 parts H_2O). Remove the excess of ammonia wash water from two of the precipitates (e) by washing 3 or 4 times with neutral 60 per cent by volume methyl alcohol solution; from two others (f) by spreading out the filter paper with its precipitate on coarse absorbent filter paper for a couple of minutes and then on to a watch glass and dry for one-half hour at 50° C. (if 60° C. is exceeded the determination must be discarded); from the last two (g) by air drying the opened out filter paper with its precipitate over-night at room temperature. Immediately after the removal of the ammonia as directed in each case, transfer the filter paper with its precipitate to a beaker or flask; moisten the paper with H_2O; add an accurately measured excess of standardized 0.10 N H_2SO_4, thoroughly disintegrate the paper and add 2 or 3 drops of methyl orange (0.1 per cent alcoholic solution). If this gives a decided pink color sufficient acid has been added. Dilute to about 100 cc. with H_2O and determine excess of acid by titrating with 0.10 N. NaOH to a clear yellow color without any suggestion of pink. One cc. of 0.10 N H_2SO_4 is equivalent to 0.0123 gms. $MgSO_4 7H_2O$. Calculate the results to grams $MgSO_4 7H_2O$ for each 25 cc. aliquot and record all results in Table III, together with the theoretical value for 25 cc. of "Solution No. 1."

From these results select the procedure, either (e), (f), or (g) which gives the best results, or if two or more give equally good results, choose the one which you prefer and use it for all

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subsequent work with the volumetric method. State your choice in Table III.

SECTION IV. COMPARISON OF GRAVIMETRIC AND VOLUMETRIC PROCEDURES.

Weigh all leather charges accurately yet as rapidly as possible to prevent material moisture changes.

For "Leather No. 1" and "Leather No. 2" proceed as follows: Weigh 5.0 gms.; ash; carefully moisten the ash with H_2O; add 10–15 cc. of conc. HCl and 1–2 drops of HNO_3. Dilute to about 50 cc. with H_2O; (h) boil gently for a few minutes and without filtering off any insoluble matter, add slowly with constant stirring a slight excess of dilute NH_4OH (4 or 5 to 1). (Note: If the precipitate does not have the characteristic reddish brown color of $Fe_2(OH)_6$ and there is known to be sufficient NH_4Cl present to hold in solution all magnesium, redissolve without filtering in a slight excess of HCl, add 1–2 drops of a dilute pure Fe_2Cl_6 solution and slowly reprecipitate with NH_4OH). Filter, wash thoroughly in hot H_2O, make the filtrate somewhat more ammoniacal (about 1 cc. conc. NH_4OH), boil gently, add slowly with constant stirring 10 cc. of a saturated ammonium oxalate solution, and let stand for 1 hr. or longer on steam bath or in warm place. Wash solution and precipitate into a 250 cc. volumetric flask, cool to room temperature, make to volume with H_2O and mix thoroughly. Filter through dry double quantitative filter paper, making sure that the filtrate is absolutely clear. (Note: This procedure for filtering off the ammonium oxalate precipitate is proposed to avoid quantitative washing of the precipitate and to give without evaporation a small volume for magnesium precipitate. It also allows of making duplicate magnesium determinations on the same ash if desired). Pipette two 100 cc. aliquots of the filtrate, slightly acidify each with HCl and in each precipitate the magnesium with excess, about 5 cc., of saturated sodium ammonium hydrogen phosphate solution, using according to your choice from Section II either the cold precipitation as directed under (b) Section I or the hot precipitation as given under (d) Section II.

After precipitation over-night carry one aliquot through gravimetrically as under (c) Section I and the other through volu-

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metrically according to your choice of (e), (f), or (g) of Section III. Enter the results in Table IV. in terms of per cent $MgSO_4$-$7H_2O$ in the leather, remembering that 100 cc. aliquot of the filtrate from the ammonium oxalate precipitate is equivalent to 2 gms. of leather.

Weigh out 5 gms. each of "Leather No. 1" and "Leather No. 2"; ash; carefully moisten the ash with H_2O; add 10–15 cc. conc. HCl and 1–2 drops of HNO_3. Dilute to 50 cc. with H_2O and add to each ash solution exactly 0.0500 gms. of $MgSO_47H_2O$ measured from "Solution No. 1" with a burette. Then proceed exactly as described from (h) Section IV on, using an excess, about 10 cc., of saturated sodium ammonium hydrogen phosphate solution for each aliquot for magnesium precipitate. Enter the results in Table IV. in the space for "Leather No. 1" and "Leather No. 2" plus 1 per cent $MgSO_47H_2O$."

Weigh out 5 gms. each of "Leather No. 1" and "Leather No. 2;" ash; carefully moisten the ash with H_2O; add 10–15 cc. conc. HCl and 1–2 drops conc. HNO_3. From a burette add to each ash solution exactly 0.3000 gms. of $MgSO_47H_2O$, measured from "Solution No. 1." Then proceed exactly as described from (h) Section IV on, using an excess, about 10 cc., of saturated sodium ammonium hydrogen phosphate solution for each aliquot for magnesium precipitation. Enter the results in Table IV. in the space for "Leather No. 1 and Leather No. 2 plus 6 per cent $MgSO_47H_2O$."

SECTION V. FURTHER COMPARISON OF GRAVIMETRIC AND VOLUMETRIC PROCEDURES.

Weigh out 5 gms. each of "Leather No. 3," "Leather No. 4," and "Leather No. 5;" ash; carefully moisten the ash with H_2O; add 10–15 cc. conc. HCl and 1–2 drops of conc. HNO_3. Dilute to about 50 cc. with H_2O and proceed exactly as described from (h) Section IV on, one aliquot gravimetrically and the others volumetrically, using an excess of saturated sodium ammonium hydrogen phosphate solution (15 cc. for magnesium precipitation will practically always suffice) for each aliquot for magnesium precipitation. Enter the results as per cent $MgSO_47H_2O$ in Table V.

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SUMMARY.

From a resumé of all the above work, give your suggestions for drawing up an official method or methods for epsom salts in leather.

The committee results have been assembled in Tables I. to V.

The comments of members follow. As they were contained in considerable correspondence the comments are not given verbatim but have been summarized.

Mr. A. C. Orthmann prefers cold precipitations with standing over-night and also the volumetric method with the alcohol wash for removal of ammonia using suction. If suction is not available, he prefers drying the filter at 50° C. for one hour. Mr. Orthmann

TABLE I.

Individual Standardization Values for "Solution No. 1."

Collaborator	Gms. $MgSO_4 7H_2O$ found 25 cc. "Solution No. 1"		Gms. $MgSO_4 7H_2O$ calcd. 1 cc. "Solution No. 1"	
	Cold pptn.	Hot pptn.	Cold pptn.	Hot. pptn.
A. C. Orthmann	0.12307			
	.12506			
	.12661			
	.12219			
Avg.	.12423		0.00497	
L. A. Cuthbert	0.12174			
	.12218			
	.12174			
	.12218			
Avg.	.12196		0.00488	
F. F. Marshall	0.1242			
	.1244			
	.1240			
	.1238			
Avg.	.1241		0.00496	
R. W. Frey (1st solution No. 1)	0.12086			
	.11800			
	.12174			
	.12064			
Avg.	.12030		0.00481	
R. W. Frey (2nd solution No. 1)	0.12329	0.12351		
	.12351	Lost		
	.12373	.12063		
	.12285	.12174		
Avg.	.12334	.12196	0.00493	0.00484
Gen'l average	0.12278	0.12196	0.00489	0.00484

(Theoretical on basis of weight and analysis of MgO taken for "Solution No. 1").

(For 25 cc. = 0.12025 gms.; for 1 cc. = 0.00481 gms.)

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TABLE II.

Comparison of Cold and Hot Precipitation in Presence of Ammonium Salts.

Note:—Figures expressed as % are on an assumed basis of 2.0 gms. simply for ready comparison.

Collaborator	$MgSO_4.7H_2O$ in 5 cc. "Solution No. 1."								$MgSO_4.7H_2O$ in 25 cc. "Solution No. 1."							
	Standardization value				Found				Standardization value				Found			
	Cold pptn.		Hot pptn.		Cold pptn.		Hot pptn.		Cold pptn.		Hot pptn.		Cold pptn.		Hot pptn.	
	As gms.	As %	As gms.	As %	As gms.	As %	As gms.	As %	As gms.	As %	As gms.	As %	As gms.	As %	As gms	As %
(1) A. C. Orthmann					0.0259	1.30	0.0275	1.38					0.1235	6.18	0.1268	6.34
					.0257	1.29	.0257	1.29					.1244	6.22	.1286	6.43
Avg.	0.0249	1.25			0.0258	1.29	.0266	1.33	0.1242	6.21			.1240	6.20	.1277	6.39
(2) L. A. Cuthbert					0.0232	1.16	0.0232	1.16					0.1231	6.16	0.1180	5.95
					.0235	1.18	.0226	1.13					.1229	6.15	.1198	5.99
															.1233	6.17
Avg.	0.0244	1.22			.0234	1.17	.0229	1.15	0.1220	6.10			.1230	6.15	.1203	6.02
(3) F. F. Marshall					0.0250	1.25	0.0244	1.22					0.1237	6.19	0.1237	6.19
					0.0246	1.23	.0246	1.23					.1240	6.20	.1237	6.19
Avg.	0.0248	1.24			0.0248	1.24	.0245	1.23	0.1241	6.21			.1239	6.20	.1237	6.19
(4) R. W. Frey (1st soln No. 1)					0.0235	1.18	0.0237	1.19					0.1211	6.06	0.1206	6.03
					.0239	1.20	.0237	1.19					.1211	6.06	.1193	5.97
Avg.	0.0241	1.22			.0237	1.19	.0237	1.19	0.1203	6.02			.1211	6.06	.1200	6.00
(4) R. W. Frey (2nd soln No. 1)					0.0255	1.28	0.0254	1.27					0.1251	6.26	0.1226	6.13
					.0248	1.24	.0250	1.25					.1237	6.19	.1222	6.11
Avg.	0.0246	1.23	0.0242	1.21	.0251	1.26	.0252	1.26	0.1233	6.17	0.1220	6.10	.1244	6.22	.1224	6.12
Gen'l average	0.0246	1.23	0.0242	1.21	0.0246	1.23	0.0246	1.23	0.1228	6.14	0.1220	6.10	.1233	6.17	0.1228	6.14

(1) Choice of procedure—cold pptn.
(2) " " " —cold pptn. (See comments).
(3) " " " —cold pptn.
(4) " " " —either cold or hot pptn.

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TABLE III.

Comparison of Different Methods for Removal of Ammonia Wash Water in Volumetric Method.
NOTE:—Figures expressed as % are on an assumed basis of 2.0 gms. simply for ready comparison.

Collaborator	Standardization value 25 cc. "Solution No. 1."				$MgSO_47H_2O$ found in 25 cc. "Solution No. 1."											
					Alcohol Wash				Drying at 50° C.				Drying Overnight			
	Cold pptn.		Hot pptn.		Cold pptn.		Hot pptn.		Cold pptn.		Hot pptn.		Cold pptn.		Hot pptn.	
	Gms.	%	Gms.	%	Gms.	%	Gms.	%	Gms.	%	Gms.	%	Gms.	%	Gms.	%
(1) A. C. Orthmann					0.1246	6.23			0.1246	6.23			0.1228	6.14		
					.1246	6.23			.1246	6.23			.1228	6.14		
Avg.	0.1242	6.21			.1246	6.23			.1246	6.23			.1228	6.14		
(2) L. A. Cuthbert					0.1230	6.15			0.1212	6.06			0.1224	6.12		
					.1218	6.09			.1205	6.03			.1218	6.09		
Avg.	0.1220	6.10			.1224	6.12			.1209	6.05			.1221	6.11		
(3) F. F. Marshall					0.1224	6.12			0.1230	6.15			0.1230	6.15		
					.1230	6.15			.1236	6.18			.1230	6.15		
Avg.	0.1241	6.21			.1227	6.14			.1233	6.17			.1230	6.15		
(4) R. W. Frey (1st soln. No. 1)					0.1209	6.05			0.1209	6.05			0.1209	6.05		
					.1197	5.98			.1209	6.05			.1196	5.98		
Avg.	0.1203	6.02			.1203	6.02			.1209	6.05			.1203	6.02		
(4) R. W. Frey (2nd soln. No. 1)							0.1208	6.04			0.1202	6.01			0.1210	6.05
							.1215	6.08			.1196	5.98			.1203	6.02
Avg.	0.1233	6.17	0.1220	6 10			.1212	6.06			.1199	6.00			.1207	6.04
Gen'l average	0.1228	6.14	0.1220	6.10	0.1225	6.13	0.1212	6.06	0.1224	6.12	0.1199	6.00	0.1221	6.11	0.1207	6.04

(1) Choice—Alcohol wash with suction or drying at 50° C. for 1 hr. if suction is not used.
(2) " —Drying overnight.
(3) " —Drying 50° C.
(4) " Either one from results, but prefer drying at 50° C. for 1 hr.

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TABLE IV.

Comparison of Gravimetric and Volumetric Procedures.

% $MgSO_4\ 7H_2O$ Found.

Collaborator	Method	Leather No. 1						Leather No. 2					
		Alone		Plus 1%		Plus 6%		Alone		Plus 1%		Plus 6%	
		Cold pptn.	Hot pptn.	Cold pptn.	Hot pptn.	Cold pptn.	Hot pptn.	Cold pptn.	Hot pptn.	Cold pptn.	Hot pptn.	Cold pptn.	Hot pptn.
A. C. Orthmann	Grav.	0.24		1.51		6.43		0 52		1.42		6.72	
	Vol.	0.28		1.29		6.18		0.37		1.38		6.32	
L. A. Cuthbert	Grav.	0.29		1.23		6.25		0.34		1.26		6.31	
	Vol.	0.31		1.26		6.18		0.34		1.29		6.27	
F. F. Marshall	Grav.	0.19		1.18		6.01		0.24		1.27		6.18	
	Vol.	0.24		1.23		6.10		0.24		1.23		6.09	
R. W. Frey	Grav.	(1) 0.27	(2) 0.17	(1) 1.28	(2) 1.18	(1) 6.35	(2) 6.03	(1) 0.32	(2) 0.30	(1) 1.37	(2) 1.35	(1) 6.50	(2) 6.14
	Vol.	0.19	0.16	1.18	1.20	6.24	6.18	0.26	0.28	1.31	1.37	6.45	6.28
General average	Grav.	0.25	0.17	1.30	1.18	6.26	6.03	0.36	0.30	1.33	1.35	6.43	6.14
	Vol.	0.26	0.16	1.24	1.20	6.18	6.18	0.30	0.28	1.30	1.37	6.28	6.28
Avg. ± Error	Grav.			+0.05	+0.01	+0.01	−0.14			−0.03	+0.05	+0.07	−0.16
	Vol.			−0.02	+0.04	−0.08	−0.02			0.00	+0.09	−0.02	0.00

(1) From first "Solution No. 1."

(2) From second "Solution No. 1."

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TABLE V.

Further Comparison of Gravimetric and Volumetric Procedure.

% $MgSO_4 7H_2O$ Found.

Collaborator	Method	Leather No. 3		Leather No. 4		Leather No. 5	
		Cold pptn.	Hot pptn.	Cold pptn.	Hot pptn.	Cold pptn.	Hot pptn.
A. C. Orthmann	Grav.	4.53		3.83		6.64	
	Vol.	4.58		3.69		6.40	
L. A. Cuthbert	Grav.	4.33		3.45		6.28	
	Vol.	4.37		3.54		6.27	
F. F. Marshall	Grav.	4.21		3.36		6.30	
	Vol.	4.24		3.51		6.24	
R. W. Frey	Grav.	4.35	4.30	3.43	3.37	6.18	6.03
	Vol.	4.25	4.27	3.39	3.41	6.17	6.05
General average	Grav.	4.36	4.30	3.52	3.37	6.35	6.03
	Vol.	4.36	4.27	3.53	3.41	6.27	6.05
Greatest difference		0.37		0.47		0.61	

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considers it entirely unnecessary to carry out the determination as outlined in Section IV in reference to that part which under certain conditions specifies the addition of a few drops of dilute pure ferric chloride solution, especially as this method would mean that whenever an iron determination was required on the leather the iron determination would have to be made on a separate portion. In reply to inquiries concerning difficulties in obtaining clear filtrates from the magnesium precipitation, Mr. Orthmann stated that he used for the gravimetric method Norton alundum crucibles, their catalog No. 5205, RA 84, dense, which he found very satisfactory. For the volumetric he used 12 cm. 00 Swedish paper.

Mr. L. A. Cuthbert had difficulty in obtaining clear filtrates from the magnesium precipitate especially with filter papers and cold precipitation. The coarse crystalline precipitates obtained from the hot solutions were much easier to filter. He used No. 0, 11 cm. Swedish papers. He also states that his results by precipitating in the cold more nearly agreed with his theoretical value and consequently he used the cold precipitation with the rest of the work but since the theoretical value was obtained by cold precipitation it did not appear fair to use this value as a standard for hot precipitation. In attempting to obtain neutral alcohol Mr. Cuthbert distilled methyl alcohol twice over lime, after which the alcohol was found to be alkaline and could not be exactly neutralized with H_2SO_4. Using this alcohol low results were obtained due it is believed to an excess of H_2SO_4 in trying to neutralize it. Better results were obtained by redistilling twice without attempting to neutralize. Mr. Cuthbert states that as spattering may occur when concentrated ammonia is added to the boiling solution it would be better to add a certain quantity of dilute ammonia. He prefers the gravimetric method because time is an important factor where many determinations are made, and while his results by the gravimetric and volumetric agree very well the latter requires considerably more time. Mr. Cuthbert approves of the idea of making the solution to a certain volume and then taking an aliquot for magnesium as in most of the work they have done on epsom salts it has been found that in weaker solutions more nearly theoretical results are obtained. He suggests a gravimetric method such as outlined in Section IV,

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precipitating from hot solution by addition of a certain amount of dilute NH_4OH (1:3 or 4) and allowing to stand at least 3 hrs. before filtering.

Mr. F. F. Marshall approves of cold precipitation by the method outlined in Section IV with choice of either the gravimetric or volumetric procedure. He recommends drying at 50° C. for one hour for removal of ammonia in the volumetric method.

Chairman: Attention first should be called to the difference between the average standardization value obtained by the committee for "Solution No. 1" and the theoretical value for this solution calculated on the weight and analysis of the MgO used by the chairman in making up the stock solution for "Solution No. 1." These figures in terms of grams $MgSO_4 7H_2O$ for 25 cc. of "SolutionNo. 1" are 0.12278 and 0.12025 respectively. While these figures are not strictly comparable because of dilution of the stock solution by each member for his "Solution No. 1," the difference would seem too great and would suggest an error in common in the committee work. It may have been that the directions in Section I for standardizing "Solution No. 1" were weak in not specifying the recognized standard procedure of double cold precipitation of magnesium and thus guarding against the influence of excess of ammonium salts and precipitant. While the directions were sent out before the work was done by the chairman, some preliminary results had been obtained which gave the same results by single cold precipitation, being careful to avoid excessive quantities of ammonium salts, as by the recognized standard double precipitation. From this the latter seemed unnecessary and the directions were drawn up accordingly. These results however were not always confirmed later and it is believed now that it would have been better to have standardized "Solution No. 1" by double cold precipitation. While because of all this the absolute value of the committee results may be in question, the same can hardly be said of the comparative study of the gravimetric and volumetric procedures.

The differences between hot and cold precipitations in Table II are not material. At the lower concentration of 5 cc. of "Solution No. 1" the results by the two procedures are almose identical. With the higher concentration of 25 cc. of "Solution No. 1" there is a general, although very slight, tendency for lower results by

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hot precipitation. It may be that with the comparatively low concentrations of magnesium in Table II, which however would be the normal range for aliquots representing 2 gms. of leather, the influence of ammonium salts is not material and that the influence is just beginning to show up in some cases with 25 cc. aliquots. Probably because of convenience the cold precipitation was generally chosen by the members.

Table III shows that three methods of removing the ammonia wash water in the volumetric procedure all give practically the same results with the same operator. The committee is generally agreed that the time of drying at 50° C. for removing ammonia should be increased to one hour instead of one-half hour. Drying at 50° C. to remove the ammonia seems to the chairman to be preferred, the alcohol wash being very tedious and unsatisfactory.

Tables IV and V show in general no significant differences between the gravimetric and volumetric methods with any one operator. Table IV also shows that upon the basis of this committee work theoretical recovery of added magnesium sulphate was obtained by both procedures.

It is evident throughout most of the work and particularly in Tables I, IV, and V that the results between members of the committee are not in sufficiently good agreement. In the last table, for example, the greatest differences on three samples of sole leather are 0.37 per cent, 0.47 per cent, and 0.61 per cent. These figures are altogether too great and show that the determination of magnesium in leather, needs to be more thoroughly studied, and more rigidly defined and carried out.

As that part of Section IV which specifies the addition of a few drops of pure ferric chloride under certain conditions has come in for a good bit of criticism a word of explanation may not be out of place. It is realized that this normally would be seldom, if ever, required, but it is proposed as a simple and practical way of preventing the precipitation of magnesium as phosphate out of place in the commonly called "ammonia precipitate," which, it must be realized, would happen if there should be an excess of phosphate, either natural or otherwise, over that required for the iron, calcium, and so on present. The criticism, that the addition of ferric chloride in those cases where the iron determination on

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the leather is also required, would mean using for the latter a separate portion of leather, has no weight, because for any leathers requiring the proposed addition of ferric chloride, the iron determination if taken, as is usual, as simply the ammonia precipitate, would not be correct even if the ferric chloride were not added.

Proposals.

(1) That the following method for the determination of epsom salts in vegetable tanned heavy leathers be tentatively adopted: Ash 5 gms. of leather; carefully moisten the ash with H_2O; add 10–15 cc. conc. HCl and 1–3 drops HNO_3; dilute to about 50 cc. with H_2O; boil gently for a few minutes and without filtering off any insoluble add slowly with constant stirring a slight excess of dilute NH_4OH (1 : 4 or 5). Avoid a large excess of NH_4OH. (Note: If the precipitate does not have the characteristic reddish brown color of $Fe_2(OH)_6$ and there is known to be sufficient NH_4Cl present to hold up all magnesium, redissolve without filtering in a slight excess of HCL, add 1-2 drops of a dilute pure Fe_2Cl_6 solution and slowly reprecipitate with NH_4OH). Filter; wash the precipitate thoroughly with hot H_2O; make the filtrate somewhat more ammoniacal (about 1 cc. conc. NH_4OH); boil gently; add slowly with constant stirring 10 cc. of a saturated ammonium oxalate solution; and let stand for two hours or longer on a steam bath or in a warm place. Transfer solution and its precipitate to a 250 cc. volumetric flask; cool to room temperature; make to volume with H_2O and mix thoroughly. Filter through dry double quantitative filter paper being sure that the filtrate is absolutely clear. (Note: This procedure for filtering off the ammonium oxalate precipitate is proposed to avoid quantative washing of the precipitate and to give without evaporation a small volume. It also permits of precipitation of magnesium in a lower concentration than if the entire charge were used and of duplicate determinations if desired). Pipette 100 cc. of the clear filtrate; slightly acidify with HCl; and add at room temperature a slight excess of saturated sodium ammonium hydrogen phosphate. (15 cc. will practically always suffice and for low ash should be reduced accordingly). If a slight precipitate forms here, clear up with a

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drop or two of HCl. Add slowly, with stirring, a few drops of NH_4OH until precipitation just begins, or in case of very low ash, until slightly ammoniacal; let stand 15 minutes; then while stirring add 10–12 cc. conc. NH_4OH (Sp. gr. 0.90). Cover the beaker and allow to stand over-night.

After precipitation and standing over-night proceed either by the gravimetric or volumetric method.

Gravimetric: Filter through a Gooch crucible, preferably of platinum; wash the precipitate free from chlorides with dilute ammonia water (1 part conc. NH_4OH, sp. gr. 0.90 to 9 parts H_2O), and finally just moisten the collected precipitate with a few drops of a solution of approximately 50 per cent NH_4NO_3 in dilute 1 to 9 ammonia water. Dry the precipitate, ignite gently at first, then cover the crucible and ignite intensely over a Bunsen or Meker burner for 30 minute intervals until constant in weight. Weight as $Mg_2P_2O_7$, multiply by 2.2135 to convert to $MgSO_4 7H_2O$ and express as per cent on 2 gms. of leather.

Volumetric: Filter through close quantitative paper; wash the precipitate free from chlorides with dilute ammonia water (1 part conc. NH_4OH, sp. gr. 0.90 to 9 parts H_2O). Remove the excess of ammonia wash water either by washing three or four times with neutral 60 per cent by volume methyl alcohol solution; or by spreading out the filter paper with its precipitate on to coarse absorbent filter paper for a couple of minutes and then on to a watch glass and dry for 1 hour at 50° C.; or by air drying the opened out filter paper over-night at room temperature. Immediately after removal of the ammonia, transfer the paper with its precipitate to a beaker or flask; moisten with H_2O; thoroughly disintegrate the paper; add an accurately measured excess of standardized 0.10 N H_2SO_4 and two or three drops of methyl orange (0.1 per cent alcoholic solution). If this gives a decided pink color sufficient acid has been added. Dilute to about 100 cc. and determine excess of acid by titrating with 0.10 N NaOH to a clear yellow without any suggestion of pink. One cc. of 0.10 N H_2SO_4 is equivalent to 0.0123 gms. $MgSO_4 7H_2O$. Calculate to gms. $MgSO_4 7H_2O$ and express as per cent on 2 gms. of leather.

(2) That, since the agreement between the members of the committee on the determination of epsom salts in leather is not

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sufficiently close, this determination should be further studied, including again for reasons pointed out, single hot precipitation.

(3) That, particularly if double precipitation is shown to be necessary, it might be desirable to include in future work the determination of the minimum time of standing, aided by shaking, that would be required for complete precipitation of magnesium.

(4) That it might also be desirable to include in the work of the next committee the analysis of epsom salts.

THE EXPLOSIVENESS OF TANNERY DUSTS*

By R. W. Frey.

No doubt you have heard and, in the past few years have read, even in the newspapers, considerable about dust explosions in industrial plants. Some of you possibly have witnessed or experienced them. However, unless the subject has been brought forcibly to your attention, you are likely to be somewhat indifferent towards it, which would indeed be a mistaken attitude. Many frightful disasters have been proved positively to be the result of dust explosions. The grain handling industries probably lead in such accidents, but reports are being received from time to time of dust explosions in other industries. As an idea of the seriousness of the matter, from March, 1916 to October, 1917, dust explosions destroyed four of the largest grain and cereal establishments in the United States and Canada, killing twenty-four persons, injuring thirty-six, and destroying foodstuffs and property to the extent of $6,000,000. This was for a period of only twenty months; others have happened all too frequently. Recently an explosion in a starch factory resulted in the loss of forty-three lives and over $3,000,000 damage was done.

In fact dust explosions became so serious, with such appalling loss of life and property in the grain handling industries, that a few years ago the U. S. Grain Corporation decided to make dust explosions a subject of thorough investigation. In co-operation with the Bureau of Chemistry a grain dust explosion prevention campaign was conducted and much valuable work was done in studying and making clear the cause of these explosions and in

*(A talk given by R. W. Frey, Assistant Chemist, Leather and Paper Laboratory, Bureau of Chemistry, at the Annual Meeting of the American Leather Chemists' Association, held at Atlantic City, N. J., June 9-11, 1921.)

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devising means of prevention. The value of this work during the War alone, in saving foodstuffs, can be readily appreciated. The work was temporarily discontinued last year because of lack of funds, but it will be taken up again the next fiscal year beginning July 1, and no doubt will expand to include finally dust explosion prevention in all industries where the dust hazard may exist.

Dust explosions may be compared very readily with gas explosions. Although the particles in a dust cloud are considerably larger than the minute molecules in a gas mixture, yet the nature and behavior of each are very much alike. Just as in your automobile you must get the right mixture, so these dusts must be in suspension in the air, in proper proportions and in intimate mixture. The mixture will not explode, however, until it is brought in contact with a flame or some other source of heat sufficient to cause the dust to ignite. (Speaking about automobiles, and as an example of turning evil into good, it is understood that work is being done on the development of a dust explosion engine and I suppose before long we will all be riding in "dustmobiles"). Two theories are advanced for the resulting explosion; (1) that a distillation of flammable gases occurs when the dust becomes heated; and (2) that the explosion is nothing more than a rapid communication of flame or fire from one particle to another, depending to a large degree upon the fineness and dryness of the dust. The rapid propagation of the flame throughout the air with the very rapid combustion of the dust particles gives an almost instantaneous product of large volumes of gases and consequently of explosion effects. The ignition might be caused in many ways as by matches, lighted pipes or cigars, torches, lanterns, friction sparks, static electrical discharges, the hot filament upon breaking an electric light bulb and so on. Quite often a small explosion, which is hardly more than a puff, may occur and be followed by fire, or the concussion and disturbance from the small explosion may throw into suspension dust that has accumulated in the plant with the result that the primary explosion or "ignition," so to speak, develops or rolls up into an explosion of large proportions. In many cases where plants have been destroyed by dust explosions a series of reports, somewhat like a roll of thunder, has been heard.

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The dust explosion men while primarily interested at the time in grain dust explosions very naturally kept an open ear for explosions of any kind which might prove to be due to dust. They had representatives in various sections of the country so that one of their men could very promptly get on the job after an explosion and make a thorough investigation.

They learned many interesting things, and among the explosions which have come to their attention in other than those plants where grain or grain products are handled, such as threshing machines, elevators, flour mills, feed and cereal mills, and starch factories, may be mentioned sugar refineries, cocoa and chocolate plants, candy factories, spice works, wood-working establishments, paper mills, printing plants, shoe factories, fertilizer works, cork grinding plants and drug and herb works, and others which because of their particular interest will be mentioned later. They also, in laboratory tests, have compiled a list of dusts giving explosions, together with the pressures generated under the conditions of the laboratory test. The pressure values mean little, if anything, of course, for industrial conditions. They do, however, give a good comparison. They are arranged in descending order of pressure generated and it will be noticed that coal dust, as a standard, is down near the bottom. One point though should be made here. Do not think that just because cork dust, for example, gives only about half the pressure of wheat smut dust, that it is only about half as dangerous and requires only about half as much precaution. An explosion of cork dust in a plant might and probably would be just as destructive as would the smut dust.

The following list will give some idea of the variety of materials covered:

Kind of dust.	Pressure generated. Lbs. per sq. in.
Lycopodium	17.5
Wheat smut dust	15.9
Yellow corn	15.2
Dextrine	14.6
Tanbark	13.3
Wheat elevator dust	13.0
Wood dust	12.8
Corn starch	12.7
Sugar	12.2
Potato flour	11.7
Fertilizer	10.5
Coal (Pittsburgh)	10.1
Cocoa	9.1
Sulphur	8.8
Cork	7.4

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You will thus see what a wide variety of dusts is represented here. Under consideration of the theory of dust explosions it is not so difficult to conceive of such disasters from mixtures of readily combustible dusts. Rather recently, however, some dust explosions of a more surprising nature have occurred. In a large rubber goods plant not long ago an explosion of hard rubber dust occurred in the grinding department in which eight men were killed and property was damaged to the extent of $25,000. Up till then little consideration had been given to the possibility of explosion from rubber dust. In February 1920, a disasterous explosion occurred in an aluminum goods factory as a result of which six girls lost their lives and as many more were seriously injured. The explosion originated in the dust- collecting system used, for sanitary reasons, for collecting the fine particles of aluminum dust formed during the process of putting on a satin finish. This process consists in holding the aluminum article against rapidly revolving steel brushes. The cause of the explosion was attributed to a piece of iron wire winding itself around the blades of the blower fan, producing sparks which ignited the fine particles of aluminum dust and gave rise to the explosion. When we know of explosions of a dust from such a material which normally is not considered flammable and ignited in such a way as this, it seems high time that we treat all dusts with respect. One difficulty in industries which so far have been fortunate in escaping dust explosions is in making the men realize the terrible possibilities. Many more such illustrations, however, as the ones just given, will make the task of conversion a light one. One of the big ideas of the dust work has been to try to have the possibilities of explosions and fires from dust more generally appreciated. It is so much better to help prevent, than to come around afterwards with an "I told you so." The experiments and experiences of the dust explosion men have about caused them to look upon all dusts with suspicion. They no longer wonder how dust explosions happen, but marvel that we do not have more of them.

As part of the grain dust explosion laboratory was next to ours, we used to hear them "banging away" quite often on their dust experiments and being rather curious I prepared for trial several samples of dust from tanning materials and leather. We used

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dust from leather, sumac leaves, larch bark, oak bark, and also powdered chestnut wood extract just as received and obtained in all cases very good, or bad, explosions. From these results the idea occurred that possibly you might be interested in hearing about them. It will also be of interest to know that the grain dust laboratory has among its files, reports up to 1915 only, of fires and explosions of bark, wood, and leather dusts numbering about fifty. The list is probably quite incomplete and certainly not up to date. According to the records many of the accidents are put down as the result of dust explosions while many were simply recorded as fires or of unknown cause. The point may be very properly made, it seems, in view of the fact that many of the reports were before dust explosions had received little, if any, consideration, that possibly many of these fires might have been the result of dust explosions.

One thing that has greatly reduced the chances for dust explosions especially around the tannery or extract plant is the use of open structures or sheds and particularly for your grinding operations where you have plenty of air and circulation to carry away the dust. One point of great importance that should be borne in mind in this connection is, that with the coming of the fine, modern, tight concrete structures and in the cities where you are more confined, unless proper precautions are taken, you increase not only the probabilities of dust explosions but also the extent of the damage which may result.

A very natural question for you to ask is, how to prevent dust explosions and a very natural broad answer is by "good housekeeping." Where you can not prevent the formation of dust, keep it down as much as possible; convey it away, keep it well dampened; and do not allow dust to accumulate around the plant. Beware of open flames, matches, friction sparks and heat, static electricity, improper electrical installation, and so on. These are simply good general suggestions. Problems of dust explosion prevention are engineering ones which can be solved by careful study in conjunction with the particular industrial conditions and circumstances involved.

In investigating and demonstrating dusts for their explosive possibilities two demonstrations in particular have proved very effective. I intended to make these demonstrations for you and

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I regret very much that because of conditions here it has been deemed too dangerous and inadvisable to give them. One of these demonstrations is very simple and consists in sifting the dust through a piece of cheese cloth on to a flame. In a darkened room this illustrates very strikingly just how the dust particles rapidly propagate the flame, resulting either in fire or explosion. Also after some experiences the test enables one to form an approximate idea of the ease of ignition of the dust.

As a further illustration of the effectiveness of dust particles to carry flame may be related an incident following this demonstration given by one of the grain dust men during their war-time educational campaign. An old gentleman in the audience rose and said, "Land's sake, we used to do that years ago," and then he told how in their lumbering operations, the camp kitchen, despite all their efforts, would get full of flies. To get rid of these flies they would light some waste paper on the kitchen floor and then stand off and throw over the flame a handful of flour. The ignition of the dust particles would carry the blaze throughout the room singeing off the wings of the flies, which would then fall to the floor and could be swept out with a broom. This was what the old gentleman called "shooting the fly."

The other demonstration is the production of an actual small scale explosion. Something which you can try for yourself, if interested. It consists in throwing a dust cloud over an open flame within a confined space. For the latter a small, tight box, having a hinged lid or some other means for relieving the pressure, may be used. In one end of the box bore a small hole and at the opposite end place a small open flame such as from an alcohol lamp. When everything is ready close the box and through a tube inserted in the hole in the box blow in some of the dust to be tested, using preferably a small bellows. You can picture the box and dust as representing your plant with its dust laden atmosphere. The flame may represent a torch or any source of heat, even, possibly, a burning match as your visitor prepares to light his cigar. From your results you can imagine what might happen should the two, that is, the dust and the flame come together under suitable conditions in a plant or factory.

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THE PREPARATION OF FRESH TANNING MATERIALS FOR ANALYSIS

By H. C. Reed

Received September 24, 1921

The opinion is advanced that the present specifications for preparation of fresh and spent tanning materials (See Official Methods of the A. L. C. A. for analysis of vegetable materials containing tannin. (2) Preparation of Sample) are inadequate, and should be revised to properly cover conditions that arise with certain materials. It is the purpose of this brief article to suggest proper methods of preparation.

Divi Divi.—No great difficulty is experienced in the case of this material in selecting a proper sample for grinding from the bulk sample, but anyone who has endeavored to grind Divi-Divi to a degree of fineness sufficient to pass a sieve of twenty meshes to the inch realizes the practical impossibility of following the directions. In the mill the pods separate into two distinct portions: a fine, powdery portion that readily passes through the mill and through the screen, and a portion somewhat of the appearance of shavings which will not grind nor pass the sieve. The readily ground, fine material lies in the inner part of the pod and contains the bulk of the tannin. The shaving-like portion comes from the outer part, or husk of the pod, and contains but little tannin. In addition there is always a certain proportion of the seed which if not too small will be crushed in grinding and if small pass through the mill as a whole.

The entire sample that has been run into the mill should be collected. This includes the portion that has passed through and the portion that may remain in the mill. If the readily ground portion does not immediately pass the sieve, there is no trouble in grinding it to a sufficient fineness to permit it to do so. The entire sample is screened and both portions, the screened and unscreened, weighed, and the proportion of each to the total weight calculated. In weighing out the portion for extraction aliquot amounts of each are taken, and since there is so wide a divergence in the tannin content of the two, considerable exactness should be exercised. Incidentally, the relative proportions of fine and shavings gives one an approximate idea of the grade of the

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material, and will assist in determining the total amount required for extraction to fall within the tannin limits prescribed by the Official Method.

Valonea.—This material arrives and is sold in three distinct forms, *viz.*, beards, cups, and cups and beards mixed. With the beards no difficulty is experienced in preparation, but difficulty arises in the case of cups and mixture of cups and beards. It is quite usual in a lot of straight cups to find that the beards have broken off and are more or less disseminated through the package. If such is the case, the preparation for analysis should be identical with that of a shipment of mixed cups and beards, so that with valonea preparation we can confine ourselves to the mixture only.

The bulk sample, which preferably should approximate ten pounds rather than five, should be screened through a coarse mesh screen that permits the passage of the beard. A screen with meshes ⅜ of an inch square will be found suitable. As in the case of Divi-Divi, both the screened and unscreened portions, beards and cups, are weighed, and the percentage of each to the total calculated. Suitable amounts of beards and cups are ground separately, and the amounts of each weighed for analysis in the proportions of each to the lot. Thus, if our calculation shows 60 per cent beards, 40 per cent cups, we may take 12 grams of beards and 8 grams of cups for the 2 liter extraction. There is not the wide discrepancy in the tan content of cups and beards that exists between the husk and powder in the case of Divi-Divi. The extremes are approximately 46 per cent tan for beards and 27 per cent tan for cups, so that here too, exactness is required.

Tara Pods.—This is a tanning material that has been imported into this country from Chili in small lots, and it is not known whether any great amount will arrive in the future. It should make an excellent tanning material, giving a tannage whiter than that imparted by Sicily Sumac. The pods are thin and extremely delicate, crushing readily in the bags so that our bulk sample is composed of husk, powdery material, and seed. The preparation for analysis is, therefore, more complicated than with Divi-Divi. It is necesssary to screen the bulk sample and ascertain the proportion of coarse and fine, using a screen similar to the one used

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in the valonea, unless one is willing to grind up something like ten pounds of the material, in which case, the procedure with Divi-Divi may be followed. After getting the relative proportions of coarse and fine, both portions must be ground separately. The fine will pass through the 20 mesh sieve, but the coarse, as with Divi-Divi, will yield a certain amount that will not pass the sieve. Therefore, the percentage of unscreenable, through the 20 mesh, must be ascertained and its relation to the original coarse calculated to find the proportion to weigh for extraction.

It should be stated that the ungrindable husk portion which cannot be made to pass the sieve is, nevertheless, a good preparation for extraction as the so-termed shavings are almost transparently thin

There are other tannin containing pods that present the same problems in preparation, but the scheme suggested can be made to cover any possibility.

A problem not so easy of solution is presented in the drawing of the original sample of valonea beards and cups mixed. The difficulty arises from the fact that the various packages do not contain equivalent proportions of cups and beards. It is our custom in this case to exceed the number of packages to be opened, as specified in the Official Methods of sampling, and to make an approximate estimate from examination of the average proportions of cups and beards in the lot. Experience is practically the only guide, and governs correct sampling in general above all else.

THE DETERMINATION OF TANNIN[1]

By John Arthur Wilson and Erwin J. Kern

A rather widespread controversy has arisen over a new method of tannin analysis described by the authors in two previous papers[2] in which it was shown that the methods adopted as official both here and abroad are greatly in error, exceeding 200 per cent in some cases. Changing a method of analysis upon which millions of dollars of tanning materials are bought and sold annually is admittedly a serious matter. Were the new method to supplant the old in the sale of extracts, drastic price changes

[1]Reprinted from *J. I.* and *E. C.*, 13, 772 (1921)
[2]This JOUR., 15, 295 (1920); 16, 75 (1921)

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would have to be made and many extracts would no longer hold their present relative standings or reputation as to tanning value. Since the official methods have been clearly proved unreliable, it would seem that the new method must now be tested generally to determine whether or not it will meet all the conditions that ought to be required of a method so important. Until now its use has been restricted because the procedure as originally described was both cumbersome and time consuming, all of the first efforts having been directed exclusively to devising an accurate method. But the procedure has since been developed until it is now quite as simple as that of any method in general use. In this paper we describe the simplified procedure and also refute the objections which have been raised against the new method.

Definition of Tannin.

A thorough review of the literature shows that it has been generally agreed to class as tannin that portion of the water-soluble matter of certain vegetable materials which will precipitate gelatin from solution and which will form compounds with hide fiber which are resistant to washing. Much confusion would have been avoided in discussion by making it clear whether the criticism was directed against the definition or the method.

Changes in Procedure.

In the method as originally described, the tanned hide powder had to be washed by shaking with water for 30 minutes, squeezing through linen, and repeating with fresh water until free from soluble matter, which usually required about 12 washings. This is now accomplished with very little effort in a washing apparatus to be described later. The washed powder, after drying, was analyzed for water, ash, fat, and hide substance (N x 5.62) and the percentages of these subtracted from 100 gave the per cent of tannin in the powder. It was suggested earlier that this figure might be obtained simply by noting the increase in weight of the dry powder after tanning and washing, provided the washing operation were so conducted that no powder was lost, making the determination direct instead of by difference and increasing the accuracy for unskilled analysts. The new washing apparatus not only makes this possible, but reduces the amount of hide powder required for a determination to one-sixth.

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PRESENT PROCEDURE.

A solution of the tanning material is prepared of such strength that 2 grams of hide powder will detannize 100 cc. in 6 hours of shaking. With a little experimenting, safe limits are easily determined for all ordinary materials so that the need for repetition will be rare. For the extracts used in this work, suitable concentrations in grams per liter are 20 for hemlock, larch, oak, and sumac, 16 for gambier, and 8 for solid quebracho. The solution must be freed from insoluble matter, which may be done in the usual manner by adding kaolin, filtering through a thin paper, returning the filtrate to the paper for an hour to tan it, then discarding all liquor which has touched the paper, pouring fresh liquor onto the filter and collecting when the filtrate comes through clear. For materials which filter with difficulty, time can be saved by setting up several filters at one time. Standard hide powder,[3] or its equivalent, is extracted with chloroform to remove all extractable matter and is then freed from solvent and stored ready for use. This treatment is chiefly to remove fatty matters and it may be found convenient to treat a year's supply at once. Two grams of this powder, of known moisture content, are put into a 6-oz., widemouth bottle, 100 cc. of tan liquor added, and the whole is put into a rotating box and shaken for 6 hours. It is advisable to keep the liquor and wash water cool to guard against any tendency towards decomposition of the untanned portion of the hide powder. This matter requires attention only in hot weather.

The essential part of the washing apparatus is shown in Fig. 1 and consists of 3 glass parts fitting tightly into one another by means of ground joints. A small piece of fine filter cloth is stretched tightly over the bottom outlet of part B and is firmly secured by winding and tying strong thread around the groove. Parts B and C are then put together and the stopcock is opened. The tan liquor and hide powder, after the 6-hour shaking, are washed into part B, the liquor being allowed to run through the open cock into a beaker and returned until reasonably clear.[4]

[3]Prepared by the Standard Mfg. Co , Ridgway, Pa.

[4]This liquor must always be tested for tannin by adding, one drop at a time, a freshly prepared solution of 10 grams gelatin and 100 grams NaCl per liter. A precipitate indicates that tannin is present, in which case the determination must be repeated using a more dilute solution of the tanning material.

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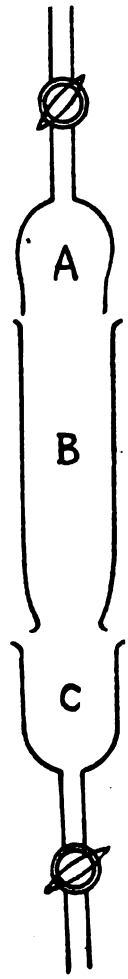

Fig. 1.

Glass washing apparatus for use in Wilson-Kern method of tannin analysis or in determination of water-soluble matter in leather. Scale 1:4.

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The stopcock is then closed and B is half filled with water and then fitted to part A with stopcock closed.

The remaining part of the washing apparatus is a reservoir of water set high enough from the table to exert a pressure equal to a column of about 4 ft. of water upon the glass receptacle, which is connected to the reservoir by means of a rubber tube attached to A. The stopcock in A is opened wide and the rate of flow of water regulated to about 500 cc. per hour by means of the stopcock in C, which is connected to the drain. Since the washing is usually complete in about 12 hours, it is convenient to start it just before leaving the laboratory in the evening so that it will be complete at the start of the next day. However, washing should not be stopped until the wash water is colorless and does not darken upon the addition of a drop of ferric chloride.

The powder is then washed onto a Büchner funnel and freed from as much water as possible by suction. It is then allowed to dry in the air over night after which it is completely dried in a vacuum oven for two hours, dessicated and weighed. It is returned to the oven and reweighed as a check against insufficient drying. The increase in weight of the dry powder represents the amount of tannin present in 100 cc. of the original tan liquor.

We have found it very convenient to have rotating boxes capable of holding 12 bottles each and cylindrical stands equipped with 12 washing devices each. Given 12 filtered liquors Monday morning, the powders would be tanned and ready for washing before evening, ready for drying next morning, and the tannin values available before noon Wednesday. With one such outfit an analyst can easily complete 12 determinations every day and still have time for other work.

Comparative Analyses.

The analyses of 6 typical extracts given in Table I show that there is practically no difference in results obtained by the original and revised procedures of the new method. Analyses by the official method of the American Leather Chemists Association, widely used in this country, are given for comparison.

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TABLE I. COMPARATIVE ANALYSES OF EXTRACTS BY A. L. C. A. METHOD AND THE ORIGINAL AND REVISED PROCEDURE OF THE NEW METHOD.

	A. L. C. A. method				New method	
					Tannin	
Extract	Water	Insoluble	Non-tannin	Tannin (by difference)	original procedure (by diff,)	revised procedure (direct)
Gambier	48.84	7.58	15.78	27.80	7.32	7.44
Hemlock	51.76	7.32	15.04	25.88	16.38	16.39
Larch	51.63	5.41	20.00	22.96	12.70	12.82
Oak	53.51	2.55	18.35	26.59	11.63	11.42
Quebracho	19.41	9.50	6.86	64.23	44.33	44.03
Sumac	49.44	2.86	22.56	25.14	13.10	13.04

DISCUSSION.

A common objection to the new method has been that it appeared inconceivable that leather chemists everywhere should have been so misguided as to accept as official a method liable to a 200 per cent error. The fallacy in the argument put forward lies in its assumption that leather chemists everywhere have found the official methods to be borne out quantitatively in practice. When data was called for to prove this assumption, apparently none was available. On the contrary, we have been able to secure data from both upper and sole leather yards showing that the amount of tannin appearing in the finished leather is very much less than entered the yards according to the A. L. C. A. method and that the apparent loss of tannin corresponds closely to the difference in tannin content of the extracts as determined by the new and official methods.

After some experimenting with the new method, Schultz and Blackadder[5] raised a number of objections to it. Their first was that it is difficult to obtain concordant results, which they explain as being due in part to the fact that the tannin was determined by difference and was subject to the errors involved in determining the water, ash, fat, and hide substance in the tanned powder. This appears to us rather a matter of skill in manipulation, but in any event the cause has vanished with the revision of the procedure.

Their second objection was that the detannized liquor and wash waters gave a test for tannin when concentrated to small bulk. In an earlier paper[6] we showed that certain non-tannins are

[5] This JOUR., 15 (1920), 654.
[6] This JOUR., 16, 75 (1921).

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converted into tannin when their solutions are evaporated and that this transformation can be followed by means of the new method, but not by the A. L. C. A. method.

Their third objection was that the degree of subdivision of standard hide powder is not uniform, that the finer portions become more heavily tanned but are more easily lost during the washing operation or in later handling, thus tending to give low results for tannin due to making the analyses on the portions of powder less heavily tanned. In the revised procedure no loss of powder during the washing is possible and all of the powder is weighed after drying. It is worthy of note, however, that the results we obtained by the original and revised procedures are practically identical.

Schell[7] has raised an objection to the method that involves the definition of tannin. Following the work of Meunier,[8] he conceives the existence of two kinds of tannin which may be likened to quinone and hydroquinone. Meunier showed that quinone has tanning properties while hydroquinone apparently has none. Given plenty of access to the air, however, solutions of hydroquinone become capable of tanning because of oxidation. According to Schell, the new method determines only the quinone-like tannin and fails to include the hydroquinone-like bodies.

But hydroquinone admittedly has no tanning properties. It seems to us that the method is all the more accurate for not including as tannin, those bodies which are not tannin, although convertible by oxidation or otherwise into tannin. The existence of these substances in tanning materials has been recognized and discussed in our last paper, in which it was shown that the tannin content of a tan liquor is increased by boiling. There is good reason to believe that the new method can be developed to determine the amount of substances convertible into tannin as well as of actual tannin. This might be done simply by analyzing the liquor both before and after some special treatment such as oxidation that will convert into tannin all substances capable of such conversion. However, the data available to us indicates that only a fraction of these substances really appear as tannin in the finished leather.

[7] *Le Cuir*, 9 (1920), 491.
[8] *Chimie et Industrie*, 1 (1918), 71.

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Schell is right in insisting that these non-tannins have a value which should be recognized in judging the value of an extract, but the values should be recognized also of those substances which aid in the diffusion of the tannins into the hides and the sugars which form the necessary acids. Two extracts of apparently the same tannin content may have very different properties. The tannin content alone is no sure guide to the value of an extract; much importance is attached to the reputation of the extract manufacturer. It is not improbable that it will eventually be found preferable to sell extracts on a basis of total solid matter, leaving the extract men to compete with each other in establishing a reputation for producing extracts of high quality and constant composition.

In speaking of hydroquinone-like bodies, Schell implies the suggestion that what the official method really determines is the sum of these and the true tannins, but this is not so. Gallic acid belongs to the class of non-tannins capable of conversion into tannin, but when added to a tan liquor only a variable fraction of it appears as tannin by the A. L. C. A. method, which makes the method quite unreliable and often very misleading. This is strikingly shown with gambier extract. The method calls for 12.5 grams of dry hide powder to detannize 200 cc. of tan liquor, which amount was assumed to be correct because the non-tannin filtrate gave no test with the gelatin-salt reagent. Using this method on a gambier extract we found 26 per cent tannin. But we then reduced the amount of hide powder to 1.5 grams; the non-tannin filtrate gave a negative test with the gelatin-salt reagent, but the per cent of tannin found was only 13. The extract is listed as containing 26 per cent tannin simply because a group of men were more favorably disposed to make 12.5 grams of hide powder official than some other amount. This is treated more fully in our first paper.

The A. L. C. A. method is based upon a principle often employed in adsorption experiments. It falsely assumes that the decrease in concentration of a tan liquor upon shaking with hide powder is a measure of the tannin content and that the solution absorbed by the substance of the hide is of the same composition as the remaining liquor. Thomas and Kelly[9] have shown to what

[9] *J. I. and E. C.*, 13, (1921), 65.

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ridiculous conclusions this can lead. In studying the effect of concentration of chrome liquor upon the adsorption of its constituents by hide substance, they had occasion to use very strong liquors. Hide powder was treated with a chrome liquor containing 14.75 grams of chromic oxide per liter, but after 48 hours the concentration had *risen* to 15.40 grams, although the hide powder had actually removed chromium from solution. This would correspond to a negative value for tannin by the A. L. C. A. method. What happened is that the hide powder absorbed a solution more dilute than the remaining chrome liquor and therefore concentrated the liquor more than enough to offset the chromium removed by combination with the hide substance. It is quite clear that one cannot determine the amount of matter removed from solution by noting the decrease in concentration of the liquor and calculating according to the instructions of the A. L. C. A. method.

Synthetic Tannins.

A representative of a firm manufacturing synthetic tanning materials of the Neradol type informed us that the use of the official method on their product meant nothing as it could be made to give any results desired. He was anxious to learn if the new method would indicate the per cent of matter capable of forming a stable compound with hide substance. While we have done no work with syntans, as they are called, it is obvious that they differ from ordinary tan liquors in that they usually contain a large amount of free sulfuric acid. In using the new method on such materials there is the possibility that the acid will cause the hide substance to swell considerably during washing. This would slow down the washing action and tend to favor decomposition of hide substance with a consequent loss in accuracy of the method. It seems possible that this might be avoided by using tap water saturated with salt for the first washings, until all sulfuric acid was removed, and then completing the washing with distilled water.

Summary.

A modification of the authors' new method of tannin analysis is described which results in a great saving of time and labor and tends towards increased accuracy.

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Objections raised against the new method are refuted.

It is shown that the principle underlying the present official methods is unsound.

A suggestion for using the new method with syntans is made.

LABORATORIES OF A. F. GALLUN & SONS CO.,
MILWAUKEE, WISCONSIN.

THE WILSON-KERN METHOD OF TANNIN ANALYSIS—A REPLY

By John Arthur Wilson and Erwin J. Kern

Received September 13, 1921.

The determination of tannin has been a controversial subject for more than a century. The need for a method has been so urgent that chemists have been impatient to devise even a questionable empirical method rather than to wait for the development of a sound chemical basis upon which to build an accurate method. Concordance rather than accuracy has been sought because, while both are essential, the chemistry of the protein-electrolyte equilibrium had not yet advanced to the point where it would serve as a guide to accuracy in tannin analysis when the present official methods were being developed. Procter's work on the acid-gelatin equilibrium led to a sounder conception of the mechanism of tanning and this in turn paved the way for the accurate determination of tannin.

The authors' new method of tannin analysis[1] is simply a further development of the work of Procter and his collaborators which has shown very clearly that the official methods are based upon an incorrect principle. Since the new method was first described, however, it has met with a determined opposition. But this is really very desirable in that it tends to bring out the truth all the more forcibly. It is hoped that this will be accomplished by the present paper, which is written in the nature of a reply to G. W. Schultz,[2] who has sought to contest the validity of the new method.

[1] *J. Ind. and Eng. Chem.*, 12 (1920), 465, 1149; This Journal, 15 (1920), 295; 16 (1921), 75.

[2] This JOURNAL, 16 (1921), 349.

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His first objection to the new method is that he was not able to duplicate his results, which he attributes to the heterogeneity of the tanned powder, the analysis of which was required in the method as originally described. The determinations which had to be made were nitrogen, fat, ash, and water. In our laboratories we have made hundreds of analyses by the new method and different analysts have had no difficulty in checking each other when working entirely independently. We are therefore forced to believe that his difficulty is not an objection to the method, but to his own manipulation or equipment.

His second objection is that his results indicate a loss of finely divided powder rich in tannin during the washing of the tanned hide powder, leaving the less heavily tanned portions to be analyzed. This, he claims, is largely responsible for the fact that the new method gives much lower results for tannin than the Official Method of the A. L. C. A. In order to test this point, we used the new method on a series of tan liquors containing no insoluble matter, but there was no difference in the results obtained whether the powders were washed as described, squeezing the wash water through linen, or by a system which prevented the loss of any matter not in solution.

In a recent paper[3] we have described a modification of the new method which results in a great saving of time and labor and tends towards increased accuracy. To make a determination of tannin, it is necessary merely to shake a fixed amount of hide powder with a solution containing a known amount of the soluble matter of the tanning material until all tannin is removed from solution, washing the tanned powder in a special device which prevents the loss of anything but matter in solution, drying the washed powder and weighing it. The increase in weight of the dry hide powder is a measure of the tannin content. Schultz's objections could not be made of the revised procedure. But the revised procedure gives results which are identical with those of the original procedure, which supports our contention that Schultz's two objections did not apply to the original procedure either, as he claimed.

An important function of a method of tannin analysis is to control the tanyard. In our earlier papers we pointed out that

[3] *J. Ind. and Eng. Chem.*, 13 (1921), 772.

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an upper leather yard can be accurately controlled by the new method, whereas the use of the A. L. C. A. Method over a period of years led to the ridiculous conclusion that half of the tanning material entering the yard was mysteriously disappearing. After asking repeatedly for figures on sole leather, we were finally rewarded with data covering a sole leather yard over a period of years. Of 100 lbs. of tannin, as determined by the Official Method, that enter the leach house, only 39 lbs. appear as combined tannin in the finished leather. Losses in the spent tan, waste liquors, and water soluble matter from the leather were determined only by the Official Method, but even with all this taken into consideration, there remains a large loss that can be accounted for only on the assumption that the Official Method gives results much too high. This does not support Schultz's expressed belief that the Official Method actually gives results lower than the true values.

The rest of Schultz's paper leads into deep water. It purports to be, but actually is not, a further criticism of the new method. An analysis of it, however, may help to clarify matters.

Among the weak points in the Official Method mentioned in our earlier work is the fact that the per cent of tannin found varies with the amount of hide powder employed. Thus the per cent of tannin in a gambier extract could be made to read anything from 13.4 to 29.0 per cent, even though all detannized filtrates gave a negative test for tannin with the gelatin-salt reagent.

Schultz now claims that this objection holds also for the new method, but let us examine the experiment upon which this claim was made. In one test he prepared a solution containing 6 grams of solid quebracho extract per liter. Five 200-cc. portions were shaken for six hours with 2, 4, 8, 12, and 20 grams respectively of air-dry hide powder. These powders were then washed 20 times and the detannized solutions and all wash waters mixed and filtered with the aid of kaolin. An aliquot of each filtrate was dried and weighed and calculated to the total volume. This amount was subtracted from the total solid matter in 200 cc. of the original liquor and the difference was calculated as tannin. In recording his results in Table I and Figure 1, we have subtracted the per cent of insoluble matter in each case. This, how-

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ever, merely lowers the curve without changing its shape. Filtration of the solution before tanning was not required in the original procedure of our method because we found that the so-called insoluble matter of ordinary extracts passed through the linen cloth in washing; at least we obtained the same results for tannin whether filtering first or not. In the revised procedure, previous filtration is required since only matter actually in solution is discarded in washing. Schultz claims that the fact that he did not obtain a straight line proves our method as objectionable in this respect as the Official Method. But his procedure was not that of the new method.

In order to show what the new method would give under the conditions of his test, we selected a sample of solid quebracho extract answering as nearly as possible the description of the sample used by Schultz. We followed the new method exactly except for using 2, 4, 6, 8, 12, and 20 grams of hide powder per 200 cc. of tan liquor in six runs. The run with two grams had to be discarded because the solution after six hours shaking still gave a positive test with the gelatin-salt reagent. We communicated this fact to Mr. Schultz, who replied that he had not made the gelatin-salt test on the solutions after the six-hour shaking. In all probability his test with two grams of hide powder should be discarded as this amount is too small to detannize in six hours the amount of tan liquor he used. We also had to discard the run with 20 grams because of the large amount of nitrogenous matter, 0.76 gram as hide substance, appearing in the non-tannin filtrate and wash waters. Standard hide powder contains a considerable amount of soluble nitrogenous matter. By shaking hide powder with water this is readily removed; if the solution obtained is filtered clear and a drop of clear tan liquor added, a bulky precipitate will form on standing. This precipitate will not be lost in the washings by the revised procedure of the new method. Where smaller amounts of hide powder were used, only a negligible amount of soluble nitrogenous matter appeared in the non-tannin filtrate and wash waters, evidently because it is practically completely precipitated by tannin, if not present in too great excess. This explains the drop obtained by Schultz with the 20-gram run. Evidently this figure should be discarded from his results also. The remaining four points obtained

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TABLE I.—ANALYSES OF SOLID QUEBRACHO EXTRACT: BY SCHULTZ USING THE PRINCIPLE OF THE A. L. C. A. METHOD, BUT WASHING THE TANNED POWDER TWENTY TIMES; BY KERN USING THE WILSON-KERN METHOD.

Grams hide powder per 200 cc.	Apparent per cent tannin found	
	Schultz	Kern
2	35.51	*
4	48.36	43.84
6	—	43.75
8	53.38	43.76
12	56.49	43.36
20	46.66	†

*Discarded because non-tannin filtrate gave positive test for tannin with gelatin-salt reagent.

†Discarded because of dissolved hide substance in non-tannin filtrate.

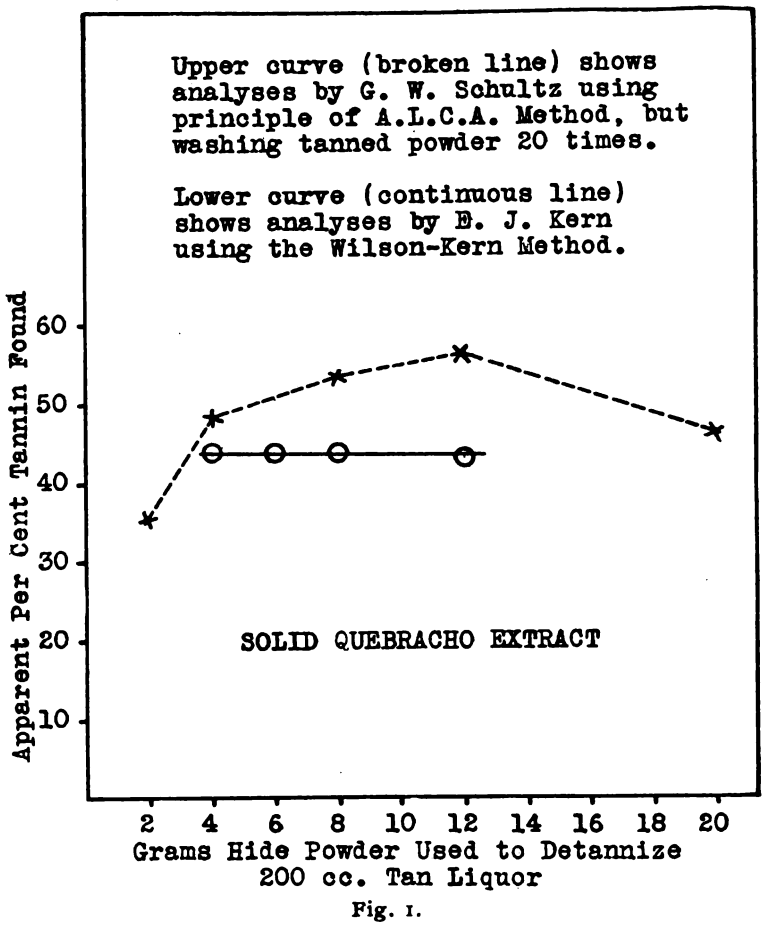

Fig. 1.

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by the new method are shown in Table I and Figure 1. It will be seen that they actually do give a practically straight line. Schultz's claim against the new method is thus shown to be false.

We are inclined to believe that, even with the procedure he did use, he would have obtained a straight line coinciding with ours, had he carried the washing to completion, as we did. More prolonged washing of the powders in our tests has no influence upon the results. Apparently only three of his points are valid, and, if washing was not complete, one would expect them to increase from the 4-gram to the 12-gram point, since more water per unit weight of tanned powder was used in washing where less powder was used.

It would naturally be more desirable to have hide powder free from soluble matter, but apparently this matter is not very serious provided sufficient tan liquor per unit of powder is used to precipitate it. Using a great excess of hide powder tends to make the method less sensitive and to favor hydrolysis of the untanned portion.

Schultz's use of extremely dilute solutions is objected to on the ground that the rate of tanning is greatly reduced and hydrolysis is favored. Six hours probably was not a sufficient time for complete tanning, but even if it were, low results would be expected because of hydrolysis. His failure to employ the gelatin-salt test in his latter work makes it quite unreliable.

We are convinced that a careful study of our earlier papers leaves no doubt that non-tannin is converted into tannin by boiling or evaporating tan liquors; it seems unnecessary to repeat what we have already written and which is readily available to anyone interested. By simply evaporating and diluting back several times, we were able to increase the tannin content of a gambier liquor, as determined by the new method, from 7.94 per cent to 12.69 per cent. That a marked change took place in this liquor cannot be disputed. A similar effect takes place during the aging of leather, but a long time is required. A sample of gambier analyzed by the new method, washing immediately after tanning, showed 7.89 per cent tannin. A portion kept 30 days before washing showed 10.49 per cent tannin, while a third portion kept a whole year before washing showed 13.13 per cent

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tannin. By evaporation, this increase is obtained in a few hours. A non-tannin filtrate which gives no test for tannin will do so after boiling. Simply exposing some non-tannin filtrates to air for a few hours will make them give a test for tannin. Schultz's experiments shaking hide powder with non-tannin filtrates do not add anything to our knowledge of this action. His statement that what he apparently found as tannin could not have been formed from non-tannin is quite without any foundation.

He leads one to infer that he questions our definition for tannin as that portion of the water-soluble matter of certain vegetable materials which will precipitate gelatin from solution and which will form compounds with hide fiber which are resistant to washing. This definition apparently was used as a guide in the development of the Official Method, although it was evidently not appreciated that the method does not determine what is called for in the definition. If we cannot define tannin, we certainly cannot determine it. Argument is therefore useless unless there is agreement upon a definition.

Schultz claims to have demonstrated that the new method is based on a series of false assumptions, but not one of his arguments intended to prove this has been able to stand investigation. On the other hand he says that the Official Method "embodies correct scientific principles for obtaining the maximum fixation of tannin," whatever that may mean. We challenge him to show that it embodies correct scientific principles for obtaining anything definite.

LABORATORIES OF A. F. GALLUN & SONS CO.,
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ON THE WILSON-KERN METHOD OF TANNIN ANALYSIS

By G. W. Schultz

In a recent paper[1] Wilson and Kern claim to have refuted the conclusions of Schultz and Blackadder[2] which were presented as reasons why the new method could not give accurate results. This claim cannot be recognized as valid. It must be pointed out

[1]The Determination of Tannin, *J. I. and E. C.* 13, 772 (1921); This JOUR., 16, 622 (1921).

[2]Some Observations on the Wilson-Kern Method of Tannin Analysis, This JOUR., 15, 654 (1920).

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that the results obtained by Schultz and Blackadder from which the conclusion was obtained that the fine particles which passed through the cloth were relatively more tanned than those which remained in it, were based on actual analyses of such material. Wilson and Kern base their claim of refutation on a modification of their method, the accuracy of which has still to be proved. Because their results with the modified method give results that check their old method does not necessarily prove that either or both are correct. The modified method is operated under a new series of conditions. The amount of hide powder, the ratio of hide powder to volume of solution, and the concentration of the solution, have all been changed. The effect of such changes has been shown in a previous paper.[3] The solution is filtered free from insolubles in the modified method which was not the case in the former method. In connection with this point it might be worth while to mention the well known fact that the insolubles in a solution of an extract increase with increase in concentration. And the increase in insolubles is accompanied by a decrease in tannin, or, the insolubles, above a certain amount that is actually insoluble in water, is formed at the expense of the tannin. Now when Wilson and Kern filter a solution of 8 grams of solid ordinary quebracho per liter they have a smaller percentage of tannin in that solution than they would have in one of official analytical strength. They would have either a smaller or greater per cent of tannin in such a solution than they would have in a solution of 18 grams or more per liter (as used in their first method) depending upon whether the insolubles in the latter solution went into solution or not upon its exhaustion by the hide powder. As an illustration of this point the following is typical:—A solution of 18 grams of solid ordinary quebracho extract per liter was prepared. A portion of this solution was filtered free from insolubles, and solutions of analytical strength were prepared from both by diluting 300 cc. to 900 cc. These were analyzed by the Official Method. At the same time duplicate determinations were made on the filtered and original strong solutions according to the original directions of Wilson and Kern. In these latter determinations all washings were collected and the

[3] Further Observations on the Wilson-Kern Method of Tannin Analysis. This JOUR., 16, 349 (1921).

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total soluble solids determined in them as a check on the method. The results are given in the following table:

ANALYSIS OF SOLID ORDINARY QUEBRACHO BEFORE AND AFTER FILTERING A SOLUTION OF 18 GRAMS PER LITER. OFFICIAL METHOD.

	Before Average of 2 determinations	After Average of 2 determinations
Total solids	82.72	69.43
Soluble solids	73.83	69.43
Insolubles	8.89	None
Non-tannins	5.07	5.14
Tannin	68.76	64.29
Tannin by W.-K. method	57.70	49.90
Total soluble solids in washings	15.53	15.22
T. S. in extract when using W.-K. method	73.23	65.12
Loss in T. S. by using W.-K. method	9.49	4.31

The effect of insolubles is apparent from the above results. It is seen that the insolubles increase from 8.89 per cent in a solution of 6 grams per liter to 13.29 per cent in a solution of 18 grams per liter. The insolubles increase by 4.4 per cent while the tannin is decreased by 4.47 per cent.

Aside from the fact that hydrolysis of the hide-tannin compound is not granted by the authors, the modified method entirely ignores the removal of soluble matter from the hide powder. A part of the soluble matter, which is common to all hide powders, is inorganic matter. Another factor in the modified method which is not conducive to accurate results is the numerous transfers of the hide powder from one receptacle to another. Even in the hands of highly skilled operators the error introduced may amount to a considerable percentage of the whole when working with such a small sample. The wet hide powder is transferred from the shaking bottle into the washing apparatus, from this into a Büchner funnel and from thence, we suppose, into a weighing dish.

Besides demonstrating that the fine particles of tanned powder which passed through the cloth were relatively more tanned than those remaining, Schultz and Blackadder also demonstrated that the tanned powder remaining in the cloth could be roughly divided into particles of three different sizes, each of which contained a different ratio of hide to tannin. In order to demonstrate that

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this result is not caused by the insolubles, tanned powders obtained with the two solutions indicated above, were divided roughly into three portions and analyzed with the following results:—

	Solution used for tanning 18 grams per liter				Same solution filtered before using			
	Average of sample	Passing 100 mesh	Passing 20 mesh	Held by 20 mesh	Average	Passing 100 mesh	Passing 20 mesh	Held by 20 mesh
Tannin per 100 Hide substance	20.19	22.12	18.85	20.21	17.46	22.75	14.63	15.95
% Tannin in Extract	57.70	63.25	53.87	57.76	49.90	65.02	41.81	45.59

Note:— The results under average were obtained by attempting to take average 1.5 gram samples of the original for analysis.

Our principal objection to the analytical determinations which had to be made according to the original method of Wilson and Kern was directed against that of nitrogen. In a private communication we were informed by Mr. Wilson that he only used 0.5 gram of the sample for nitrogen determination whereas we found that we could not extract an average portion by taking a sample three times as great. All of our nitrogen determinations were made on 1.5 gram samples. The preceding table readily presents a picture of the difficulty to be encountered in taking a fraction of such and at the same time obtaining an average. The analysts who can obtain an average 0.5 gram portion from such samples should with all propriety proclaim their skill.

In the preceding paper Wilson and Kern present some results by the new method on quebracho extract using four different amounts of hide powder. From the fact that practically the same results are obtained it is concluded that the writers claim against the new method is false. It should be pointed out that the writer did not infer that the new method would not give such results but that it should not if it were correct. It is for this reason that the procedure of determining the amount of soluble matter in the washings was adopted since it was recognized that it would give results that could be relied upon as being very nearly accurate. The point that is raised that there is tannin in the filtrate when using 2 grams of hide powder is good and is as it should be. For it is the writer's contention that the reason for the sharp increase in absorption under these conditions is due to the fact that much tannin remains in the solutions with the lower amounts

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of hide powder, disregarding the fact that the gelatin-salt solution will not precipitate it, for this reagent has not proved quantitatively reliable. The cause attributed for the low result with 20 grams of hide powder does not seem justifiable. The same results were not obtained with the chestnut extract and the writer doubts if the drop in the curve at 20 grams would be obtained under different conditions with quebracho, as it is entirely contrary to all known results when using wet hide. Moreover, a correction was applied for soluble matter that could be removed from the respective amounts of hide powder. It also should be mentioned that the ferric chloride test was applied to all of the washings in the work referred to and it was found that the wash waters from all of the powders tanned with quebracho failed to give a coloration with this reagent before the 15th washing was reached, which fact, according to Wilson and Kern, demonstrates that all of the nontannins had been removed and that washing was complete. Under such circumstances the objections of Wilson and Kern to the results obtained by the writer are not valid.

The definition given by Wilson and Kern will serve in a broad and general way as a definition of tannin, although it must be remembered that gelatin will not be precipitated by tannin under all conditions, moreover there are chemical compounds known which will tan hide but which will not precipitate gelatin. There are also different degrees of resistance to washing. It is the writer's opinion that the new method fails when it assumes that hide will quantitatively remove tannin from any given solution, and that a negative test with gelatin-salt reagent, given by a solution after treatment with hide powder, can be accepted as proof of such.

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RECOVERY OF ACETIC ACID DURING THE EVAPORATION OF TANNING EXTRACTS*

By Georges Vie

France has nearly a monopoly in the manufacture of chestnut-extract. During the war 35 plants were actively operated. Thanks to the work of Schoen the acetic acid contained in the chestnut

*Translated for *J. A. L. C. A.* from *Le Cuir*, 10, 329 (1921).

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wood and volatilized during evaporation of the liquors can be recovered by a procedure simple in theory but rather capricious in practice. (Editor's note: The recovery of acetic acid is not due to Schoen but to Mitscherli, who conceived the idea first in 1878). From a purely chemical viewpoint the recovery of acetic acid is a simple operation but from the cost standpoint at the present time it may be contested on several points. During the war the need for acetic acid made its recovery desirable.

The installation of the washing apparatus for the vapors has been an onerous task. Aside from the questions of the metal for the apparatus, the corrosion which occurs, and the discoloration of the product, it should be remarked that the construction of the apparatus has not received due consideration. Logically the washer or scrubber should be of copper since otherwise the accidental or mechanical entrainment of some of the tan liquor will upon mixing with the sodium acetate result in a decided discoloration. At the time of installation however copper was not available and means were provided to prevent this contamination. It should be emphasized though that since it is desired to recover the sodium acetate as white as possible a scrubber which serves at the same time as a retarder and trap can not be satisfactory.

From the production of 1000 kgs. of 25° Bé chestnut extract 13.2 kgs. of acetic acid may be recovered. The consumption of sodium carbonate (95 per cent) for this would be 12.25 kgs., giving 59.8 kgs. of saturated sodium acetate solution of 21° Bé. This saturated solution is decanted and evaporated in the air in a double boiler. The concentration is continued until the boiling point of the solution reaches 125° C. The fused acetate is then run onto a screen in thin layers and upon cooling is broken up. The 59.8 kgs. of 21° Bé sodium acetate solution yield from this treatment 23.84 kgs. of acetate, composed of 18 kgs. of anhydrous sodium acetate and 5.84 kgs. or about 1.5 molecules of water of crystallization. The acetate intended for the chemical plants for military purposes during the war was to be delivered in this form but the installation of the recovery apparatus in the extract plants was too late to be of any help, only one or two factories producing acetate before the armistice. The sodium acetate with

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1.5 molecules of water of crystallization does not have a definite crystal form being intermediate between the anhydrous and crystalline acetate.

The production of the acetate at 125° C. can be accomplished with sufficient facility with steam at the usual pressure of the extract evaporators which rarely exceeds an average of 4 kgs. The fused acetate can be poured into plates which are very convenient for packing. The product should be sold in the crude state on its moisture content, it being understood that the product should be perfectly neutral and completely soluble. If the boiling at 125° C. has been thorough the product should contain 75.2 per cent of dry material.

To secure a neutral solution of sodium acetate in the scrubber is rather difficult. The addition of a little lime during the decantation not only precipitates the iron and tannin impurities but produces a partial decolorizing effect and a very slight alkalinity. The temperature of the boiling of the acetate is quite important if one wishes to obtain a product which is uniform and dry upon cooling. To reach the boiling point of 125° C. requires steam at 3 kgs or at 134° C.

It is proposed to discuss in the near future the construction and operation of the apparatus for recovery, at present it is desired to digress a little on the possible manufacture of acetate of lime instead of sodium acetate. During the first half of last year it was difficult if not impossible to secure sodium carbonate in sufficient quantity at a reasonable price. An attempt to substitute lime was therefore made. The milk of lime is used in the same way as the sodium carbonate solution, but a lime of high purity is required. The limes usually contain a large proportion of unburned and insoluble material which complicates the operations and increases the evaporation because of the necessity of using weak solutions. The expense of evaporation becomes excessive, the decantation is not rapid enough to keep pace with the production of the plant, and the product of sodium acetate, which could be very good because of the decolorizing action of the lime, has a dirty appearance. The use of sodium carbonate gives about 20 kgs. of sodium acetate from 1000 kgs. of 25° Bé extract while with lime the yield of calcium acetate is about 12.5 kgs.

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The lime requires more acetic acid than the sodium carbonate, 100 kgs. of calcium acetate corresponding to 165 kgs. of sodium acetate. Recovery by lime requires less material.

R. W. F.

ABSTRACTS

Precipitation of Proteins by Tannins. By T. Sollmann. *J. Pharm. Exp. Ther.*, 16, 49—59 (1920). The precipitation of proteins by tannin depends on the reaction of the medium. In solutions of the concentration (0.1—0.5%) necessary to produce astringent action precipitation is greatest at $p_H = 2$—5. There is no precipitation when the alkalinity is $p_H > 8$—8.3. The precipitation limits are the same for Witte's peptone as for egg albumin and serum-albumin, and for extracts of catechu as for ordinary tannin. Gallic acid produces, within the same limits, only slight precipitation, probably due to contamination with tannin.

J. S. C. I.

2.4.6-Trinitroresorcinol (Styphnic Acid). By H. Einbeck and L. Jablonski. *Ber.*, 54, 1084—1089 (1921). Styphnic acid, m. p. varying from 174° C. to 179°—180° C., is obtained by the oxidation of quebracho extract with nitric acid (sp. gr. 1.4). For its characterisation the mono- and di-potassium salts have been prepared by the regulated addition of alcoholic potassium acetate solution to styphnic acid dissolved in alcohol, and the mono- and disodium salts by the use of alcoholic sodium hydroxide. All the salts, the mono-sodium compound in particular, explode violently when heated.

J. S. C. I.

Gallotannin. XII. By M. Nierenstein, C. W. Spiers and A. Geake. *Chem. Soc. Trans.*, 119, 275—286 (1921). Further evidence obtained on the constitution of gallotannin seems to throw doubt on the correctness of the pentadigalloylglucose formula of Fischer and Freudenberg. The formation of ellagic acid from gallotannin occurs in two distinct stages, the first producing a maximum of 60 per cent, and the second giving only traces of ellagic acid, but about 8 per cent of dextrose. Similarly, partially hydrolysed gallotannin gave ellagic acid in two distinct stages, whereas from the pentadigalloylglucose formula simultaneous production of ellagic acid and dextrose would have been expected. Further, the methylated derivative of the above partially hydrolysed gallotannin, and also of gallotannin itself, gave on hydrolysis tetramethylglucose. These results are fundamentally opposed to the pentadigalloylglucose formula, since apparently four hydroxyl groups of the glucose in gallotannin are free unless the methylation with diazomethane had caused a replacement of the acyl groups, which, however, was shown to be excluded by the fact that dextrose, and not tetramethylglucose, was formed

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by the hydrolysis of the methylation product obtained by the action of diazomethane on a synthetic pentagalloylglucose.

J. S. C. I.

Extraction of Gallotannic Acid. By E. Knape. *Chem. Zeit.*, **45**, 239—241 (1921). Galls are swollen with water, ground, and extracted with ether or ether and alcohol for 20—30 mins. in a cylindrical shaker fitted with an agitator. The extract is filtered off and three more extractions made. A clearer, brighter solution is obtained in this way than from dry powdered galls, and less solvent is required. Saturating the solvent with water and using this for the extraction of powdered dry galls is not so successful. The ether may be replaced by trichloroethylene or dichlorocthylene with equally good results.

J. C. S. I.

The Properties of Gelatine. By L. Meunier. *Le Cnir*, 10, 313-331 (1921); *Chimie et Industrie*, **5**, 642 (1921). Because of its amphoteric character gelatine unites with either acids or bases to form salts, which dissolved in water, and are completely ionizable. Gelatine salts of acids are however quite different from the metallic gelatinates. For example, the reaction between gelatine and hydrochloric acid is reversible while that between gelatine and sodium hydroxide is not. It might be conceived that under the action of acids the CO.NH groups take the keto form -CO-NH, giving keto salts while with bases they take the enol form $-C(OH)=N-$, give enol salts which could explain the above difference.

Data on the constitution of gelatine are rather limited. The values for its molecular weight differ so widely that hardly any can be accepted. The oldest figure (Schutzemberger and Bourgeois, 1876) being 1836 and the most recent (Jordan Lloyd, 1920) 10,300. Among the hydrolysis products of gelatine it should be recalled that glycocoll forms a large proportion, also some phenylalanine but no tyrosine. Gelatine does not respond to Millon's reagent. Contrary to the opinion of Diaminovitch and Gugliamelli the author has obtained a compound with gelatine and nitrous acid, stable in the dark, which reacts with phenols giving colored products (Richards' reaction). The reaction is more pronounced with skin than with gelatine. Dilute solutions of gelatine because of the high degree of dispersion are excellent protective colloids, the gold figure varying from 0.005 to 0.01, while for albumin and gum arabic it ranges from 0.15 to 0.25 and for dextrin from 6 to 20.

The work of Dhere and Gorgolewski (*Compt. Rend.*, 1910, 150, 934) showing the influence of electrolytes, as impurities in the gelatine, upon its electrical charge, is summarized, as are also Jacques Loeb's studies (*Jour. Biol. Chem.*) dealing with the influence of electrolytes and of the hydrogen ion concentration on the properties and reactions of gelatine solutions. The important bearing of the hydrogen ion concentration on the properties

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of gelatine makes desirable some practical means of determining the former and the usual colorimetric procedure for determining hydrogen ion concentrations with indicators and comparator tubes is described as very satisfactory.

A summary or digest is given of the work of Hardy (1900) and Bradford (*Biochem. Jour.*, 12, 382, 1918) on the structure of gelatine gels; of Procter, Procter and Burton, Procter and Wilson, Loeb and Jordan Lloyd on the swelling of gelatin; of Larguier des Bancels (*Comp. Rend.*, 146, 290, 1908) on the action of alkali and alkali-earth salts on gelatine; and of Luppo Cramer (*Zeitsch. Chem. Ind. Kolloids*, 4, 21, 1909), Lumiere and Seyewetz (Bulletin *Soc. Chim.*, 743, 1908), Meunier and Seyewetz (*Monit. Scientifiq.*, D. Quesneville 91, 1909) on the tanning of gelatine with the halogens, mineral salts,, and organic compounds.

R. W. F.

Contribution to the Study of Sole Leather for Army Shoes. BY JALADE. *Halle aux Cuirs*, Aug 21, 1921. 229—38. Schiaparelli's article (*J. S. L. T. C.*, Feb., 1921) on the testing of sole leather, destined especially for army shoes, is discussed in the light of experiences of the French laboratories for examining military supplies. There is, first of all, an important difference between Schiaparelli's procedure for preparing the samples to test their permeability by water and that used by the French laboratories. By the former all samples are first submitted to the same pressure under rollers in order to obtain the same compactness, whereas by the latter they are tested as received regardless of the amount of rolling they have had. Like Schiaparelli, Jalade believes that a low water soluble content does not always improve the intrinsic properties of sole leather. Very often low water soluble content corresponds with a high permeability.

It should be noted that the loss in weight, as defined by Schiaparelli, by total immersion in water for 72 hours does not correspond with the value obtained by the procedure in the specifications of the French military authorities. The latter, it is believed, represents a mean between the former and the value by extraction with the Koch apparatus, which is so generally used in England and America and which, because of the temperature of the extraction, has too severe an action on the leather (*Le Cuir*, 15, 1919).

The influence of soaking on the thickness of the leather has been noted by both authors. A sample of leather, for example, which had an original thickness of 5.3 mm. measured 6.8 mm. after a short soaking and drying in the air for 48 hours. A few leathers return slowly to their original thickness, while others retain indefinitely the added thickness from soaking. The increase is generally about 10 per cent. It is known that hammering causes a loss in thickness from the "crust" state of 15 to 20 per cent so that the effect of hammering or rolling is often nearly removed by a simple immersion in water. It can be conceived then that the soaking, so indispensable to the shoemaker, can appreciably increase the permeability of the leather.

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Schiaparelli's suggestion that the "actual coefficient" of permeability should be practically one-half of the coefficient from total immersion, since only the grain side of the sole comes in contract with the moisture of the ground, is not acceptable. Using an apparatus (*Le Cuir*, 71, 1920) in which the grain side only is subjected to a column of water, fixed for these experiments at 20 cm., it is proved that contrary to general opinion, the grain side absorbs very rapidly the water which comes in contact with it and the absorption is practically the same as by the flesh side. In a few seconds the grain absorbs nearly 57 per cent of the quantity necessary to entirely penetrate the leather. A possible explanation of this is the high degree of tannage of the grain. Furthermore, while it may seem paradoxical, results have been obtained with the above apparatus showing, in a given time, a permeability by absorption through the grain, greater than indicated by weighing before and after immersion, taking into account the loss by material washed out in the latter method. Data to show this are given on two leathers, one of average permeability and one of low permeability. The "actual coefficient" of permeability by the immersion method is about one-third and the coefficient of total permeability about two-thirds that by Jalade's apparatus. The total immersion method is therefore at fault and besides does not approach actual conditions. Permeability should be considered from two viewpoints; the capacity to absorb and the time for penetration. A leather thoroughly wet will wear away rapidly and the time required to dry may constitute a menace to the wearer. Concerning the second point the time of penetration is independent of the initial thickness: thus, a leather of 6 mm. thickness is penetrated in 15 minutes and absorbs 1.9 cc. of water; another of 4 mm. absorbs 2.1 cc. before being penetrated in 1 hour; and a third of 4.2 mm. absorbs only 1.7 cc. and is not penetrated in 24 hours. Furthermore the thickness after soaking and drying is often greater than the original thickness, yet in this condition a repetition of the test requires less water and time for penetration.

Jalade does not entirely agree that the permeability is inversely proportional to the soluble matter. This may be influenced by the particular characteristics of the tanning materials used. Furthermore the resistance to water due to excessive quantities of soluble materials will prove a poor practice since with each wetting of the leather some of the soluble materials will be removed and the permeability will be rapidly increased. It is considered that when the soluble material is about 14 to 15 per cent, on the dry, grease-free leather, the resistance to water is satisfactory if at the same time the degree of tannage is about 70. Numerous experiments have shown that mixed tannages, after proper plumping and laying away for two to three months, produce generally sole leather, of satisfactory resistance to water. Leathers of rapid tannage, while responding well to the test at first, became permeable after a few immersions. Such leathers are generally heavily loaded with soluble materials and have a low degree of tannage. Slow tannage sometimes produces leathers of

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too great a permeability because in addition to a low degree of tannage they are often improperly oiled. An experiment by Schiaparelli emphasizes the importance of the degree of tannage on the permeability. It shows that a leather immersed in water 72 hours and thus thoroughly washed, when returned to the tan vats for two months has a much better resistance to water. There is no doubt that the additional tanning increased the degree of tannage which was originally too low and at the same time rendered insoluble an appreciable quantity of the tannin which then acts as a cement in the interfibrillar spaces.

R. W. F.

The Action of Sodium Carbonate on Chrome Alum Solutions. By L. MEUNIER AND P. CASTE. *Le Cuir*, 10, 290–2 (1921). In previous work (*J. S. L. T. C.* 1921, p. 103 and This JOURNAL, 16, 321) considerable data on the reactions between sodium carbonate and chrome alum are given including some results on old solutions at constant temperature. Further experiments are now described on the titration of sodium carbonate and chrome alum solutions maintained rigidly at a constant temperature and in diffused light, the observations being started immediately upon dissolving the chrome alum. It develops that the reaction is more complex than appeared at first, there being involved two phases of unequal duration. The first is relatively short, lasting a few hours or days, during which time the quantity of sodium carbonate required for the appearance of a permanent precipitate increases to a maximum varying with the dilution and temperature. The second phase is relatively long, lasting several weeks and even months during which time the quantity of sodium carbonate regularly decreases to a minimum. The first condition is longer and more pronounced with greater concentrations and lower temperatures.

The following titration values are given: Five-tenth per cent chrome alum solution maintained at 14.5° C. in diffused light. Solution complete in 4 minutes. Fifty cc. aliquots titrated at intervals given below with 0.1 N sodium carbonate at practically 14.5° C.

Time	Cc. 0.1 N sodium carbonate
4 mins.	6.9
8 "	8.8
15 "	9.6
20 "	9.9
43 "	10.0
68 "	10.2
80 "	10.2
6 hours	10.2
7 "	10.2
24 "	10.4
48 "	10.4
5 days	9.7
10 "	9.4

Five per cent chrome alum solution maintained at 15° C. in diffused light. Solutions complete in 30 minutes. Ten cc. aliquots titrated at intervals given below with 1.0 per cent sodium carbonate at 15° C.

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Time	Cc. 1% sodium carbonate
30 mins.	5.5
55 "	5.7
1 hour	5.8
1.5 "	5.0
2 "	6.0
2.5 "	6.1
4.5 "	6.1
5.5 "	6.3
7.5 "	6.5
14 hours	6.7
22 "	8.1
28 "	9.1
39 "	9.9
44 "	10.0
49 "	10.0
3 days	9.8
5 "	9.5
10 "	9.2

Comparing these results with observations by other workers on the electrical conductivity of chromium sulfate solutions at constant temperature, it will be noted that the minimum conductivity corresponds probably with the maximum titration values given above, that is, at the lowest degree of ionization more sodium carbonate is required to start precipitation. This relation may be explained by the influence of two distinct phenomena. As soon as the chromium sulfate is dissolved it undergoes partially an immediate hydrolysis. The chromium hydroxide thus formed is at first peptised by the non-hydrolyzed normal chromium sulfate and is maintained in colloidal solution. The hydrate and sulfate then slowly unite to a complex in which the chromium hydroxide is not so susceptible to the action of sodium carbonate. If this phenomenon alone occurred the ionization would continually decrease with time and the amount of sodium carbonate for titration would thus increase. As this immediate hydrolysis is not instantly complete, further hydrolysis occurs liberating more chromium hydroxide which becomes more and more difficultly peptised so that its colloidal solution is more sensitive to the action of sodium carbonate, with the result that ionization increases and the quantity of sodium carbonate for precipitation decreases. This theory is in accord with results obtained in previous studies.

R. W. F.

Osmosis and Swelling of Gelatin. By C. R. Smith. *J. A. C. S.* **43**, 1350 (1921). The experiments were conducted on ash-free and electrolyte free gelatin which is prepared as follows: Ten grams of finely powdered gelatin (about 16 mesh) is placed in a 24 cm. folded filter supported at the tip by a cone or small funnel, and the whole in turn placed in a funnel of suitable size (15 cm.). A 10 per cent sodium chloride solution con-

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taining about 5 cc. of conc. hydrochloric acid per liter, cooled to between 0° and 10°, is poured back and forth several times through the powdered gelatin. Fresh portions of the salt-acid mixture are then used until no test for lime can be obtained in the washings. This acid mixture is then replaced by cold 1 per cent salt solution without acid, and washed back and forth. From now on, the concentration of the salt solutions is diminished as rapidly as control of the swelling will permit. If the salt washings were discontinued the gelatin might swell and occupy the whole filter, making washing extremely difficult. Preferably the gelatin should be permitted to swell no further than two-thirds up the filter. A considerable washing will be required with very dilute salt solutions and finally with distilled water until no chlorine is found in the washings, when the gelatin particles will have contracted to a volume of about 7 or 8 cc. per gram of gelatin. It is advisable to continue the washing with several liters of distilled, aerated-distilled, or conductivity water, if high purity is to be ensured. Finally cold 90 per cent alcohol is poured through the drained jelly masses until they are shrunk nearly to dryness, after which they are dried with an electric fan. Ash-free gelatin thus obtained contains no ash except traces of sand when the original gelatin contains such. When ashed with pure sodium carbonate, chlorides, sulfates or phosphates cannot be detected. It swells in water at 15° to about 7 or 8 volumes. If such be melted and cooled a clear stable jelly is produced. Syneresis takes place in a weaker jelly than this with production of a cloudy jelly. A 0.5 per cent jelly will flocculate into jelly particles and can be filtered off from the water which shows no trace of gelatin. Ultimate analyses of the ash free gelatin gave the following average:—C, 50.52; H, 6.81; N, 17.53; O, 25.15.

Ash-free gelatin dissolved in warm water, placed in collodion thimbles, cooled to 10°, and immersed in water showed no osmotic pressure. When the jellies are melted at 35°, pressures proportional to the concentration are obtained. Assuming the applicability of the gas laws, a molecular weight of about 96,000 is obtained.

Gelatin sols in a collodion membrane immersed in isohydric solutions of univalent acids, or polyvalent acids ionizing as a univalent acid produce the same osmotic pressure. When immersed in solutions of univalent bases the same osmotic pressure is produced at the same hydroxyl-ion concentration. With increasing hydrogen- or hydroxyl-ion concentration the osmotic pressure increases to a maximum and then diminishes. The maximum osmotic pressure for 0.5 gr. of gelatin per 100 cc. at 10° in univalent acids or polyvalent acids ionizing as univalent, is reached at a hydrogen-ion concentration of 0.8 to 1.0 $\times$ 10^{-3}, and amounts to about 158 mm. of water. In univalent bases the maximum is reached at 0.2 $\times$ 10^{-8} hydroxyl-ion concentration and amounts to about 165 mm. In bivalent acids or bases ionizing as such the maximum osmotic pressure is reached at the same hydrogen or hydroxyl-ion concentration as with univalent acids or bases, respectively, but only amounts to 55 mm., or about one-third as much.

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When dry gelatin is immersed in univalent acids, or polyvalent acids ionizing as univalent, it combines with equivalent amounts at the same hydrogen-ion concentration. The amount of swelling is approximately the same for all, its maximum occurring at about 4×10^{-3} hydrogen-ion concentration when one gram of air dry gelatin occupies a volume of about 46 cc. Bivalent ionizing acids give much less swelling with a maximum at about the same point, and combine in somewhat greater equivalent amounts. When ash-free gelatin is immersed in dilute sodium chloride or potassium bromide solution, no diminution in concentration can be detected. It is doubtful if salt ions combine with gelatin but they increase the absorption of alkalies or acids. They decrease swelling and osmotic pressure, probably by decreasing the ionization of acids or alkalies combined with the gelatin. Since salt ions do not appreciably affect the ionization of the dilute highly ionized mineral acids or bases, the hydrogen or hydroxyl ion is not the determining factor when salts are present. The action of buffer mixtures likewise is not determined by the hydrogen-ion concentration. The author considers the swelling of gelatin as the result of osmotic pressure within the jelly, with the jelly acting as an imperfectly resisting membrane the more so when highly swollen. While the osmotic pressure at the optimum concentration of univalent acids and bases is the same, the swelling is much less in alkalies because of the weakened membrane effect. Bivalent sulfuric acid gives the same swelling as bivalent calcium or barium hydroxide when swelling is small and the solution is not so great. Experiments with ash-free gelatins of low jellying power gave the same osmotic pressure as those of the highest power but they swell much less, the swelling being proportional to jellying power. The author takes exception to Procter and Wilson's assumption that the hydrogen-ion concentration of the jelly is always less than that in the external solution. Moreover, he concludes that it appears incorrect to consider a lump of jelly or the liquid contents of a collodion sack as a phase distinct from the surrounding liquid. The bulk of the enmeshed liquid in the jelly or sack has the same concentration of electrolytes as the exterior liquid.

G. W. S.

Shaving Leather by Machine. By A. Wagner. *Gerber*, **46**, 97 (1920). A description of the proper care and manipulation of shaving machines. The appearance of shaved leather, known as "ribby" ("Treppen") can be caused when the shaving cylinder has an eccentric motion owing to worn bearings, etc.; when the machine is not on a firm foundation; when the operator does not put sufficient weight on the foot lever; when the blades of the knife roll are not firmly in the grooves; or when the leather is not fed to the knives at the optimum rate. The advantages of an automatic leather feed and a double width working-roll shaving machine are given.

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Electro-Osmotic Tanning. ANON. *Gerber*, 46, 107 (1920). Previously, the many patents for tanning with electricity were not successful because the electric current was introduced directly into the tan liquor. Destruction of the tannin occurred through oxidation without obtaining a noteworthy tanning effect. German Pat. No. 283,285 and subsequent patents of the Electro-Osmose Akt.-Ges. protect a process for tanning with a direct current, by placing the electrodes in diaphragms immersed in the liquor thus preventing decomposition of the tannin. A vat like container separated by 2 diaphragms into 3 parts is used for tanning. The middle space in which the hides are hung is filled with tanning liquor of about 2° Bé. The exterior spaces are filled with water and in these hard lead poles are placed. A vat of about 2 x 2 x 2.5 meters will serve for 25-30 hides and require a current of 110 volts and 90-100 amperes. With the use of high percentage tanning materials 20-30 hours and a current consumption of 20-30 Kilowatt hours are required for a full tannage.

To overcome the high price of electricity, this process was combined with the use of the old tanning process so that the consumption of current was reduced to about one sixth of the above amount. The hides are given an 8 to 10 hour electric tannage, followed by treatment in handlers in the normal way when leather of good yield is obtained in from 12 to 30 days depending upon the kind of tanning material used. Two samples of belting leather tested by the deutschen Versuchsanstalt für Lederindustrie in Freiberg analyzed as follows:

	Per cent	Per cent
Water	15.5	15.5
Mineral matter	0.5	0.5
Fat	13.9	14.1
Organic loss on washing { Tannin	1.9	0.3
Organic loss on washing { Non-tannin	0.9	1.4
Leather substance { Tannin	29.5	31.8
Leather substance { Hide substance	37.8	36.4
	100.0	100.0
Yield number	264.6	274.8
Degree of tannage	78.0	87.4
Sp. gr. (average of 5 samples) = 0.81		
	Sp. Gr.	
	Neck	0.939
	Middle	0.931
	Flank	0.926
Breaking strength—2.9—3.0 kg. per sq. cm.		2.6—3.0 kg. per sq. cm.

G. W. S.

Researches on the Processes of Tanning—IV. BY W. MOELLER. *Ledertechn. Rund.*, 13, 57 and 67 (1921). An investigation of the effect of acids when used in conjunction with tanning material which was executed with hide power along the same lines as noted in previous papers of this series. Twenty cc. of solutions of hydrochloric acid of N/10, N/2 and N/1 concentrations were added to a series of 4.4 grams portions of

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absolutely dry hide powder and allowed to stand for 1 hour when 980 cc. of solutions of quebracho extract of about 1% and 3% concentrations were added and allowed to stand for time intervals of 1, 8, and 14 days, 3 weeks and one month. Another series was carried out in the same manner using solutions of hydrochloric acid varying from N/1000 to 6 N after which a solution of 6% quebracho was added. Still another series was carried out with 20 cc. of solution of acetic acid of N/100, N/20, N/10, N/2 and N/1 concentrations followed by 980 cc. of 6% quebracho solutions. To determine the amount of material absorbed by the hide powder a correction for the amount of material precipitated by the acid from the solutions of various concentrations was applied. It was found that for quebracho solutions, the amount precipitated by hydrochloric acid apparently quickly increased with increase in concentration of acid until a maximum was reached which was different for each concentration of tanning material. Acetic acid gave practically no precipitation at the concentrations used. It is concluded that the previous swelling of the hide powder gives a greater adsorption of tanning material when either hydrochloric or acetic acids are used than was obtained in previous experiments with quebracho extract under the same conditions without the use of acids. The use of acetic acid gave relatively greater adsorption of tanning material than was obtained with the use of hydrochloric for the same concentrations. A slighly greater hydrolysis of the hide substance was obtained by the use of acids but this was more than offset by the increase in adsorption of tanning material.

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Researches on the Processes of Tanning—V. By W. Moeller. *Ledertechn, Rund.*, 13, 81 and 97, (1921). An investigation of the effect of acids when added together with tanning material to hide powder. Mixtures of solutions of quebracho and solutions of acids were made to give the concentrations desired. These were allowed to stand for 24 hours and the supernatant liquid siphoned off. 1000 cc. of such solutions were added to 4.4 grams of hide powder and after standing for time intervals of 1, 8 and 14 days, 3 weeks and 1 month, were tested for nitrogen and solids. The first series was run with a 6% quebracho solution containing hydrochloric acid in concentrations of from N/1000 to 6 N. Another series with 1% and 3% solutions of quebracho containing hydrochloric acid in concentrations of 2 N, 4 N and 6 N. A final series was run with 1%, 3% and 6% solutions of quebracho containing acetic acid in concentrations of 5 N and 10 N. From the results of these experiments the author concludes that with a 6% solution of quebracho adsorption of tanning material is retarded with the lower concentrations of hydrochloric acid, from N/1000 to N/1 when compared with the same strength solution containing no acid, while there is no appreciable decomposition of the hide substance. With the higher concentrations of hydrochloric acid there is an enormous increase in nitrogen in solution and at the same time an enormous increase in the

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amount of tanning material adsorbed, especially with increase of time, and this increases with increasing acid concentration. The two increases are correlated by the assumption that the hydrolyzing effect of the acid on the hide substance increases the surface of the hide and thereby increasing amounts of tanning material are adsorbed. With the 1% and 3% quebracho solutions there is a relatively greater decomposition of hide than occurred with the 6% solution. The 1% solution giving the largest values for nitrogen in solution especially at the higher concentration and at the greatest time interval. While the adsorption values are the greatest for the 3% and least for the 1% solutions. The experiments with the large amounts of acetic acid showed that decomposition of the hide was increased but was practically negligible when compared with that caused by hydrochloric acid.

G. W. S.

The Identification and Examination of the Tanning Materials and Extracts. By R. Lauffman. *Ledertechn. Rund.*, 13, 65 and 73 (1921). The vegetable tanning materials are divided into two main groups, depending upon the properties of their tannins as derivates of catechin and pyrogallol. In a third group is classed those materials whose tannin content consists of a mixture of these derivates. The tannins of quebracho wood; pine, mimosa and mangrove barks; gambier and catechu belong to the catechol group. Those of oak and chestnut woods, valonea, divi-divi, myrobalans, sumac and knoppern belong to the pyrogallol group, while those of oak, chestnut and willow barks belong to the mixed group. The presence of sulfite cellulose extract and also treatment of the extracts with sulfite interferes with some of the tests used in the examination of the materials and therefore the presence or absence of such must be determined before considering the results of an examination. An abnormal ash is often an indication of treatment with sulfite which can be confirmed by adding a few drops of sulfuric acid to a hot dilute solution of the extract when the odor of sulfurous acid is obtained. Sulfite cellulose is tested for by the Procter-Hirst reaction and the reaction with cinchonine sulfate. [See This Jour., 13, 438 (1918).]

A solution of one per cent gelatin and 10 per cent salt is used to indicate the presence of tannin. A solution composed of 200 cc. of 10 per cent ferric chloride solution, 15 cc. of 10 per cent sodium acetate solution and 10 cc. of 50 per cent acetic acid is used as a qualitative test. When several drops is added to a solution of tanning material of analytical strength a green coloration or precipitate is given by the catechol tannins with the exception of mimosa bark, (with extracts it is often olive to brown). With pyrogallol tannins, mimosa bark, mixed tannins and their extracts a violet color or precipitate is obtained. Artificial tanning material also give the coloration with the iron salt solution. To distinguish between pyrogallol and catechol tannins and detect mixtures of these the formaldehyde and hydrochloric, and the bromine water re-

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actions are of prime importance. *Reaction with Formaldehyde*:—Twenty-five cc. of a solution produced by mixing 100 cc. strong HCl, 100 cc. water and 150 cc. 40 per cent formaldehyde is added to 50 cc. of clear tannin solution, boiled under reflux, cooled and filtered. Catechel tannin and sumac give a precipitate. The filtrate is tested for pyrogallol tannins by adding 4-5 drops of a 1 per cent solution of iron alum, mixing and adding some solid sodium acetate. Pyrogallol tannings give a violet colored zone with this test. *Bromine Water Reaction*:—To 5 cc. of a clear solution of the tanning material is added the same volume of 0.5 per cent bromine water. Catechol tannins give a precipitate, pyrogallol tannins do not. Sulfited extracts or extracts containing sulfite cellulose extract will hinder or prevent the precipitation of catechol tannins. In the presence of such materials failure to give a precipitate with this test does not prove the absence of catechol tannins. *The Reaction with Lead Acetate in Acetic Acid Solution.* To 5 cc. of the solution of tanning material 10 cc. of 10 per cent acetic acid and 5 cc. of 10 per cent normal lead acetate solution are added. The pyrogallol tannins are more or less precipitated and the catechol tannins are not. *The Color Reaction with Garancine Strips*—Twenty-five cc. of the filtered solution of analytical strength is diluted to 1 liter with hot water, heated to boiling and a Garancine strip placed in it. The solution is boiled for ½ hour, continuously replacing the evaporated water, the strip is then removed from the solution and dried. Another strip is placed in the boiling solution for a half hour and this is continued until from 5 to 7 strips have been used and the solution is nearly exhausted. The color of the dried strips must be compared with colors produced by extracts of known purity. The color difference produced by pyrogallol and catechol tannins is decided and the method is suitable to detect mixtures of the two as the pyrogallol tannins color the first strips and the catechol the last. Strongly sulfited extracts give colors that are more or less different from that of the original. *Sulfuric Acid Reaction*:—Eight to 10 drops of the tannin solution is added to about 2 cc. of concentrated sulfuric acid on a watch glass and stirred quickly with a glass rod. Quebracho wood and mimosa bark extracts give a strong carmine red; divi-divi gives a red; pine, oak and mangrove bark extracts, oak and chestnut wood extracts give a brown to reddish brown; myrobalans, valonea, knoppern, gambier, catechu give a brownish yellow to yellow; and many mangrove bark extracts give a dirty violet coloration. *Pine Shaving Reaction*—A smooth pine shaving is placed in a solution of 4 times analytical strength, removed after 15 minutes, dried and moistened with concentrated HCl, gambier or catechu give a purple red or violet coloration. Other materials give none or only weak colorations. *Test with Molybdenum Reagents*:—The reagent is prepared by mixing equal volumes of a 10% solution of ammonium molybdate and 15 per cent solution of ammonium chloride. [For a description or the procedure and results see This Jour., **15**, 435 (1920).] *Determination of the Formaldehyde Precipitation Number*—[See This Jour., **13**, 222 (1918).] *Acetic Ether Solubility Number*:—Twenty-five cc. of the filtered tannin solution is shaken out with 25 cc. pure acetic ether until the acetic

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ether extract remains colorless (3-4 times). 20 cc. of the extracted tannin solution and 20 cc. of the original solution are evaporated to dryness. The difference is calculated to parts per 100 part dried residue in original solution. This number is lowered by sulfiting extracts. *Extracts of the Catechol Group*:—Quebracho extract is recognized by its low molybdenum number (0-35), high formaldehyde number (80-110), high number for acetic ether soluble (70-85), and the reaction with sulfuric acid. Mimosa bark extract is recognized by a fairly high molybdenum number (60-90), a high formaldehyde number (80-130°), fairly low number of acetic ether solubility, a violet color with iron alum in contrast to the characteristic green color of this group of tannins and a carmine red color with its sulfuric acid reaction. Mangrove bark extract gives high molybdenum numbers (100-130), high formaldehyde numbers (70-100°), low acetic ether numbers (0-20°) and a brown or dirty violet color with sulfuric acid, mangrove extracts are also characterized by a high content of sodium chloride. Pine bark extract, gives medium molybdenum numbers (20-40), formaldehyde number (40-44), low acetic ether numbers (10-25) and a brown color with sulfuric acid. Gambier is characterized by a purple-red or violet color with the pine shaving reaction, very low molybdenum numbers (0-10) and a brownish yellow color with sulfuric acid. Catechu gives a deep violet color with the pine shaving reaction, very low or no values for the molybdenum number and a brown color with sulfuric acid. *Extracts of the Pyrogallol group*:—Oakwood extracts give low formaldehyde numbers (10-20), low acetic ether numbers (5-25), high molybdenum numbers (100-160) and a brown color with sulfuric acid. Chestnut wood extracts give low formaldehyde numbers (5-20), low numbers for acetic ether (20-50), high molybdenum numbers (140-200) and a brown color with sulfuric acid. Chestnut wood extract is distinguished from oakwood extract by its greater purity and lower ash content when it is not treated. Divi-divi, myrobalans, valonea and sumac give higher acetic ether numbers, with the exception of valonea (30-60) than do oakwood or chestnut wood extracts. The formaldehyde numbers lies between 5 and 15 with the exception of sumac which gives higher values. *Mixed Tannin Extracts*:—Oak bark extracts are distinguished from oak wood extracts by their higher formaldehyde numbers (40-60) and lower molybdenum numbers (65-85).

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CORRECTION

Attention is called to the following errors in the proposed Provisional Methods for the Analysis of Sulphonated (Sulphated) Oils, published in the October number of This JOURNAL:—

Page 527, lines 28 and 29—Per cent Neutralized combined SO_3 =

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1.49 × (Per cent combined.....etc., should read.....Per cent Na_2SO_4 in ash due to combined $SO_3 = 0.0634$ [2C + (F + A)], when 2C > (F + A) substitute (F + A) for 2C. Line 33—Per cent Salts and impurities in Ash =; should read Total salts and impurities in oil =.

Page 528, line 3, the word Ash should be omitted.

NATURE AND ESSENTIAL CHARACTER OF THE TANNING PROCESS AND OF LEATHER*

[Translated for *J. A. L. C. A.* from *Collegium* Nos. 589 and 590, 133 and 166 (1919), and published by courtesy of the Editor.]

By Friedrich Knapp

The process of finding explanations for the phenomena met with in everyday life by means of a knowledge of natural science, is going on at the present time on a very extensive scale but the demand for such explanations is far greater than can be met. At times, theory is brought to bear on a particular branch of knowledge in consequence of demands imposed by such branch, or is enticed into such an investigation by the interest which the practical branch offers for a nearly related scientific discussion. At other times, such a branch remains less regarded by science because of lack of external stimulus, or because of the difficulty which investigation may expect to encounter by reason of the unfavorable nature of one or another of the materials in question. Also because of confounding of the unusual with the important, scientific research has often been deflected from things of the most radical importance and applied to the insignificant. Thus it happens that we know more about the scientific manufacture of ultramarine than about the thousand year old manufacture of glass; that we know better a number of exotic drugs than rye or barley flour; that more researches have been made on upas poison than on the kinds of fruit or on chicory coffee; that we possess no clear scientific knowledge of the nature of cast iron, steel, porcelain and many similar things. Few industrial branches which are of importance because their products are prime necessities of life have remained so far beyond the cognizance of science as is the case with tanning. Truly, science has essentially enlarged the knowledge of tanning materials but it has occupied itself with-

* In response to many requests, this classic work of Friederich Knapp, which appeared in 1858, published by the J. G. Cotta Buchhandlung, but which has been out of print for a long time, is now reprinted in the *Collegium*. Since the subject matter of this treatise is still of active interest in technical circles to-day and more recent researches often refer to it, the reprint is justifiable and will be gladly received by our readers.

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out agreement, more completely with the chemically than with the technically important tanning materials such as oak bark. As much as it has clarified the chemical nature, the constitution of the tanning materials, still the knowledge of its relation to animal hide, of the mutual action of both and the nature of the resulting products, has experienced a proportionately insignificant increase.

Tanning is of purely empirical origin and has grown out of the practice of manual operations. The different methods of tanning are perhaps not branches springing from a common stem by rational development, but have simply originated in different regions. The national stamp of the industry, according to the means of manufacture available is prominent frequently in present day practice. One speaks of Hungary leather, of Russian leather; chamois tannage was originally only the tannage which the hunting Indians and breeders of cattle performed with the brains or fat of dead animals; tanning with gall nuts, morocco manufacture, is the tanning method of the Orient; tanning with oak liquor that of the occident, etc. According to that which our present knowledge offers it is still very difficult to form a clear conception of the nature and essential character of leather and of tanning. Much is not in harmony with the facts in general; much that is appropriate for bark tanning, is not so for tawing, that which is reconcilable to this, is not so for chamois tanning and vice versa.

Séquin, who has made valuable investigations on tanning, defined leather as industrially produced gallate of gelatin, which he bases on the change of animal fiber into gelatin by boiling water as well as on the great affinity of the latter for tannin. Animal hide is not gelatin, although indeed, capable of being changed into gelatin by boiling; the compound of gelatin with tannic acid is hard and brittle and the object of tanning, above all else, is to retain the flexibility of the hide. The compound of aluminum salts with gelatin acts similarly. It is also seen from the definition of Séquin that it is not applicable to chamois tanning, it is also not tenable for bark tanning and tawing. Prechtl states, in his *Technologic Encyclopedia*, Vol. IX, p. 238; "the imputrescible substance combines (in tanning) with the fiber so that this loses its capability of fermenting by virtue of this chemical combination."

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Later authors no longer speak explicitly of a chemical combination of the fiber and tanning material. Thus Dumas (*Chimie appliqué aux arts,* Vol. VII, p. 523) states: "combiner la matiére animal de la peau avec le tannin" Berzelius, *Jahrbuch,* Vol. IX, p. 369 speaks merely of a "union" of both without further elucidation, while Kamarsch and Heeren, *technisches Worterbuch,* 2nd Ed., Vol. II, p. 561, state: "leather is formed by definite modes of chemical treatment."

More recent authors appear again to consider leather as merely a chemical compound. Johnson (*Dingler's polyt. Jour.,* p. 145, 167) states, in the description of his method for making glue from leather wastes: "as long as tannic acid is combined with gelatin in the leather." Pagen, in his treatise on the more intimate constituents of leather (*Dingler's,* 145, 70) declares: "the strength of leather is dependent on the property of two tannin compounds which had been formed in the same hide" one non-fibrous and one fibrous; he states further: "tannin combines with both parts of the hide, the non-fibrous and the fibrous,[1] for each of the same, much smaller amounts of tannin are necessary than for gelatin." Stenhouse in a communication on producing gelatin from leather (*Dingler's polyt. Jour.,* 147, 70) speaks of the "difference of constitution" between sole and upper leather, of "a change (on account of which dried leather no longer yields gelatin) which depends more on a rearrangement of the molecule than on the loss of nitrogen."

It therefore appeared of sufficient interest for theory as well as practice to make a series of observations in order to establish to some extent, conceptions on the nature of leather.

It is known that it is not hide, in the widest sense of the word, that the tanner works, but purified hide or pelt, that is, corium which has been freed from all extraneous formations and material, if not completely, still in a high degree. The purified hide has the same condition in the wet state as on the animal body; it exhibits a milky white, very soft, flexible texture, which under the microscope, consists of extremely delicate, colorless, transparent, ramifying forked fibers which in general run parallel to the hide surface. The opacity and milky white appearance has only an optical basis due to the dispersion of light. On drying,

[1]This distinction coincides well with the tissue of the hide and the animal fluid matter, which is in the hide in life and is not absolutely removed on tanning.

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this texture contracts to a horny, transparent, apparently structureless, homogeneous mass, which after being placed in water for some time swells again to the previous flexible, milky white hide.

The phenomenon of the hide losing its milky white appearance on drying depends on the fact that the connective tissue fibers and elastic fibers agglutinate, in a manner somewhat analogous to the twisting of the intestinal coating for musical instruments, so that there are no interspaces and light dispersion is prevented. The strength with which the fibers adhere to one another is so great that it is impossible to effect their separation in a purely mechanical way, and thereby give the hide again its original flexibility in the dry state; it remains either stiff, parchment like, and tears, or resists tearing as thicker cattle hides do. If purified hide remains for a time in water there ensues a putrescent odor and an evident disappearance of its substance; it becomes thinner and later shows perforations which increase more and more until at last the whole is destroyed.

The different operations of tanning, taken in the most general meaning, have a twofold object; first to abolish as much as possible the tendency of the hide to putrefaction; secondly, to give the hide the property, not of a stiff horny mass after drying, but of a distinctly fibrous, non-transparent, more or less flexible texture, which easily allows it to be altered without strain by mechanical means. A hide that does this is called tanned (gar) and the technical term tanning (Gerben)[2] derived from it is significant, as, from the point of view of the artisans, first and above all the point in question is of the finished state (die Gäre) regardless of the means of obtaining it.

For attaining both of the prime objects of tanning, each of the three main operations, cleansing the hide, tanning, in its narrow sense, and finishing, have an influence, but the second operation, tanning, has the greatest; nevertheless, it is necessary for consideration of this latter to consider some points in

Cleansing.

The subcutaneous tissue attached to the flesh side of the hide as well as the fine blood vessels and nerves permeating the tissue

[2]Properly "Gärben" from gar machen.

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of the hide, at least the substances impregnating them, will be removed by the known means of soaking and working on the fleshing beam. Cleaning of the grain side, unhairing, is, however, characteristic; it aims at the anatomical separation of the corium from the superimposed epidermis and structures connected with the latter, especially hair. The phenomena and methods of manipulation involved in unhairing have been often misunderstood[3] because the anatomy was not considered. Hair, as is known, is purely a epidermal structure and is only seated indirectly in the corium, directly, however, in a pocket of epidermis projecting deep into the corium. The means used in unhairing (lime in liming, decomposition in sweating) therefore only aim at the loosening of the epidermis. The scraping off of the hair from limed or sweated hides, in reality, only consists of taking the epidermis and the hair fixed in it from the corium; the hair serving much like a handle. This is effected somewhat differently by the use of Rhusma[4] or similar acting sulphur compounds. As Böttger in his time had observed, the product of the action of hydrogen sulphide on milk of lime has the same action on the hair and in the same degree, as the mixture of arsenic sulphide with dissolved lime; at the same time it is excellently suited to the close observation of the process. If milk of lime be saturated with hydrogen sulphide then there is formed besides the undissolved calcium sulphide a water-clear solution of calcium sulphhydrate, which alone possesses the action of Rhusma. If a hair be immersed in such a solution, then it is completely softened after a few seconds, loses its transparency, becomes milky and is crushed with ease by the gentlest pressure. If the softened hair be observed under the microscope it is found that the exterior cell layer which surrounds and envelopes the hair has completely disappeared and the otherwise firmly bound fibers of the true hair substance are separated from one another and softened. If a piece of hairy hide be treated in a similar manner, the hair can be scraped off with a wooden knife. However, the epidermis is not simultaneously removed and the hair is more superficially removed than uprooted.

[3]Thus, for example, Prechtl states in his *Encyclopedia*, Vol. 9, p. 244: "the hair is rooted in the subcutaneous tissue."

[4]Originally used to designate a mixture of nine parts of lime and one part of red sulfide of arsenic. Translator.

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TANNING.

How the union or combination of the hide with the tanning substance shall be conceived if it is not chemical, remains an important question for theory and practice. If one runs through the very long list of patents and improvements on the subject of tanning then one must confess that a not inconsiderable part of the endeavor to use and to make progress through the incorrect observations in vogue, has had no useful result. Thus a patent exists, to quote only one example, wherein the inventor of a rapid tanning method sought to make the interior of the hide accessible to tannin by perforating the hide before tanning, on a machine, with needle points! The hide is now so permeable and in such a degree accessible to the tannin that a piece of a 1-1½ line calf hide placed in a syrupy etheral solution of nut gall tannin is completely and fully tanned in an hour at the most. The customary procedure of the tanner also contains not a little that contradicts the hypothesis that leather may be simply a chemical compound If leather were a chemical compound of the gelatin-yielding hide substance with tannin, then other gelatin-yielding animal matter should form leather just as good, which is not the case. Fibers of delimed bones for example, after prolonged treatment never form anything similar to leather. Conversely, aluminum and iron salts possess marked tanning properites, although they do not precipitate gelatin. Further the difference in the chemical nature of tanning materials and their multiplicity is none too favorable to that assumption. Salts of the metallic oxides M_2O_3, tannic acid, fat are such heterogeneous things and still produce in the tannery such similar effects. If a body of organic origin of some one histological form, for example, in the form of fibers, etc., combines with any other chemical, as a rule it takes place with the loss of this form, that is, the compound is no longer fibrous. It is true that in the case of gun cotton the fiber enters into a true chemical combination with nitric acid with the retention of its organic form but at least the combination is not reversible, which is the case with leather. With hide the anatomical structure and the form of the connective tissues not only are not attacked by tanning but are rendered more distinctly prominent. It appears that the tanning material fixed on the hide is held completely as chemically free; in this fixation it is easily

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capable of combining with any other body, for which it has affinity, as, for example, tannic acid fixed on the hide is colored black with iron salts, etc., without being freed from the fiber. A hide tanned in gallotannic acid and then washed in a large quantity of water and for a long time, yet has uncombined tannin remaining in the pores. Digested in the cold with a very dilute solution of sodium carbonate, the originally water clear solution assumes a brownish yellow color, which rapidly darkens in contact with the air, it precipitates ferric salts, tartar emetic and gelatin. The residual part of the leather, appears transparent and swollen, it dries after the washing to a translucent, horny mass which in boiling water is gradually but completely decomposed to gelatin. This is also a complete transformation of leather into hide and thus hide can be changed any number of times into leather and reverted. If a leather tanned in oak liquor be treated in the same way, considerable is extracted by the soda solution as indicated by its brown coloration. Iron salts blacken this solution at first but not after standing. The residual leather appears likewise swollen, much lighter in color than previously, but still it is leather, it does not yield gelatin, a reduction to hide does not occur. Therefore the unfortunately little known tannin of oak bark (of which we only know that it is very different from that of gall nuts,) must adhere more intimately to the fiber than gall-nut tannin.[5]

As tannic acid on the hide can be changed and can combine chemically with other matter, so also can the hide fiber alter without freeing tannic acid. If leather be boiled in water, it is not material in this case whether it is bark or gall nut tanned, then it is changed into a deep brown (in the hot) tough, ropy, (in the cold) brittle, easily powdered, fiberless mass of conchoidal fracture, a substance which is nothing else than a compound of tannin with gelatin. Alum tanned leather acts entirely like hide, boiled in water it changes without more ado into gelatin which is dissolved; placed in acidified water, it swells like hide and is not to be distinguished from such. This is not the case with bark tanned leather. Every tanner knows that tawed leather

(5) This observation has been mentioned six years previously in my Chemical Technology. Also Stenhouse (*l. c.*) found on treating leather with calcium-hydrate in an autoclave, that certain light leathers were reduced to hide, but sole leather never. He believes this circumstance, which perhaps only depends on the difference of tanning material used, must be sought in a difference of "constitution" of the kinds of leather.

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should not be washed after tanning. Alum tanned leather especially gives up fairly rapidly and completely the absorbed aluminum salts on washing with cold water, so that at the end nothing remains but the original hide. With alum tanned or tawed leathers therefore a chemical combination of aluminum salts with the hide fiber is the lease tenable assumption. Such an assumption is far more probable in the case of the constituents of chamois leather, which shows in fact a remarkable resistance to reagents. Boiled for a long time in water it yields only traces of gelatin and after drying retains its fibrous properties and flexibility almost unchanged, only that it becomes somewhat cracky on the grain, provided it had been tanned with the grain on. Only by treatment with a solution of caustic alkali, if it is not treated until completely dissolved, will chamois leather become brittle and cracky after drying. Acids do not swell it at all. If all of these experimental facts be summarized for a decision of the question, whether leather is a chemical compound of hide with tanning material or not, then they speak on the whole against it. Still the question is open for experimental solution. It appears to be of particular interest to study the influence which the hide (connective tissue fiber) exerts on the tanning material, whether it is capable of producing decomposition of it, in what amounts by weight it takes up the material. To that end the hide is exposed to a solution of tanning material of known content and the result investigated. It would seem at first sight the simplest to weigh the hide before and after the tanning experiment but it is impossible to obtain even approximately correct results in this way. It is always very difficult to bring the hide to such a high degree of purity that it no longer gives up soluble matter to the solution of tanning material, and it is not much easier to dry the hide completely for the purpose of weighing without at the same time making it unsuitable for the absorption of tanning material; but above all the tendency of the hide when washed to part with the tanning material which it had taken up offers the greatest obstacle. Since the limit is not definitely marked, one always remains in doubt as to whether a part of the tanning material fixed on the hide is again removed by too drastic washing, or whether on the contrary there has been left in the pores of the hide a part of the non-fixed tanning material

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by deficient washing. For the experiment, hide cleansed by the tanner, so-called pelt, is procured. It is first wrung out, soaked in distilled water and wrung out again, and continued three or four times in order to free it completely of soluble constituents by methodical washing. To this end the tallest possible glass cylinders serve the best; these are filled with distilled water and the piece of hide placed in the cylinder by means of platinum wire or glass rests so that they are just immersed below the surface. That which the distilled water dissolved from the hide sinks to the bottom and is immediately replaced by pure water. With 5-10 grams of hide it is sufficient to renew the distilled water in the glass cylinder every 24 hours, four or five times in order to attain the point where a test dried in vacuo no longer shows a decrease in weight. The changes which the hide produces in the solution of tanning material, can be best observed in the solution itself. For treatment of the purified and washed hide with the tanning material, the solution of suitable strength is placed in a thin beaker of 150-200 grams capacity, which can be weighed on a sensitive balance. The beaker is capable of being closed at the top with a ground-on glass plate as a cover. The slight evaporation, which occurs in spite of the glass cover during the period of the experiment, can thus be controlled very exactly with the balance; a glass rod as stirrer for moving the hide is included. In this manner one is in position to control every change in weight of the whole. The quantity of that which the hide absorbs and fixes from the solution, is obtained from the analysis of the solution before and after the experiment, calculated on its quantity. By this laborious and time consuming manner, which in many cases can be shortened by titration, the action of hide and tanning substance can be studied in the act of their mutual combination without the lest disturbing interference.

Tanning Experiment with Alum.

In 40.655 grs. of a dilute solution of ordinary, repeatedly recrystallized alum is placed for 48 hours with frequent stirring a piece of calf pelt of 3.862 grs. dry weight which has been completely washed in distilled water. The washed hide was first dried between absorbent paper and then in vacuo over sulphuric acid, weighed, afterwards soaked up in distilled water and added

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together with the latter to the alum solution, while the increase in weight produced thereby was determined. The alum solution before the experiment weighed 40.655 grs.; 19.822 grs. of the same gave 0.225 alumina, corresponding to 1.132 anhydrous alum; the solution after the experiment weighed 40.164 grs.; 13.984 of this gave 0.144 alumina and 0.408 sulphuric acid, corresponding to 0.690 anhydrous alum. There was therefore:

Before the experiment 2.318 grs. anhydrous alum
After the experiment 1.983 grs. anhydrous alum
in solution and therefore 0.335 grams or 8½ per cent of the weight of hide had been fixed. The hide appeared completely tanned. The quantities of sulphuric acid and alumina found are in the proportion of 4 SO_3 :1.08 Al_2O_3 and therefore no change in composition of the aluminum salt has taken place.

When alum solution was treated many times in succession with strips of hide and then evaporated, the liquid yielded only alum crystals as before tanning.

TANNING EXPERIMENT WITH ALUMINUM SULPHATE.

Under the same conditions as in the previous experiment 1.814 grs. of purified hide were brought into 41.996 grs. of a solution of pure aluminum sulphate. The solution contained 1.589 dry salt before tanning, after tanning 1.082 grs. and therefore there was fixed by the hide 0.507 or 27.9 per cent; 24.103 grs. solution before tanning gave 0.262 gr. alumina and 0.591 sulphuric acid; after tanning 10.006 grs. solution 0.114 alumina and 0.259 sulphuric acid. The equivalent ratio in the first case is 1 :2.92. in the second case 1 :2.91, also unchanged and no decomposition has occurred.

TANNING EXPERIMENT WITH ALUMINUM CHLORIDE

1.386 grs. hide, purified by washing and dried in vacuo is placed in 29.093 grs. of a solution of aluminum chloride produced by precipitation of aluminum sulphate with barium chloride, which in 100 parts by weight gave on analysis:

	I	II and III	Mean
Alumina	3.86	3.39	3.625
Silver Chloride	29.73	29.97	29.76

This value corresponds to a ratio of 1 equivalent of alumina to 2.94 of silver chloride. After 48 hours the solution gave in 100 parts:

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Alumina	1.84	1.95
Silver Chloride	14.99	14.87

corresponding to 1 equivalent of alumina to 2.92 of silver chloride. Here also the composition has not changed, while a strong reaction of the hide on the liquid occurred. The content of aluminum chloride in the liquid is calculated as:

Before the experiment	1.744
After tanning	1.365
And therefore	0.379 or 27.3 per cent has

been fixed. By washing in distilled water according to the method designated above, the hide still contained after three days 3.46 per cent, which without doubt would also be removed by continued washing.

Tanning Experiment with Aluminum Acetate.

1.139 grs. pure hide is digested with 6.565 grs. of a solution of aluminum acetate produced from sugar of lead and aluminum sulphate.

This gave before the experiment	0.432 gr.	
after tanning	0.166 gr.	ignition residue or alumina.
therefore	0.266 gr.	has been fixed by the

hide corresponding to 23.3 per cent.[6]

One would err, if he were to believe, that the aluminum salts combine always in the same proportions given here. On the contrary, the circumstances, that they again give up fixed salt to water, makes it very probable, that they absorb more in concentrated solution and less in dilute, as has been confirmed by experience.

Above all, it has been found from these experiments that aluminum salts have not been absorbed in equivalent proportions, for example:

	Equivalent	Amount of salt absorbed
Alum, Anhydrous	258.6	11
Aluminum Chloride	133.6	27.3

that here the aluminum salts have been absorbed not in constant quantity but in amounts, which vary according to exterior conditions, concentration etc.; that, finally, on absorption of the

[6] This number is somewhat too great since some specks of coagulated aluminum salt were visible on the hide.

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salt by hide fiber no decomposition occurs and a basic salt is not fixed on the hide while an acid one remains.[7] As is known, aluminum chloride is not used in practice for tanning but a solution of alum with common salt in varying proportions (19 to 130 and more per cent of the alum). It appears, that the salt is more than merely a means for converting aluminum sulphate into chloride, indeed its true activity is found in another direction. If in a comparative experiment the same hide is tanned with solutions of different aluminum salts, then a very great difference will be noted. Aluminum sulphate is farther removed from giving a serviceable and flexible leather under the same conditions than a solution of alum with salt. When three similar samples of calf skin were placed into solutions at the same time and for the same length of time, the first test in a solution of alum alone, the second of alum with salt, the third of red liquor;[8] all three solutions containing the same amount of alumina, then the leather of the second test alone was tanned through and flexible, that of the latter was the worst, which is so much the more striking as acetic acid is by far the easiest acid to part with alumina. It is beyond doubt that common salt in tawing exerts an individual and very active influence, partly as a substance actively promoting endosmose, partly because in solution it has an action on hide similar to that of alcohol, of which more will be said later.

Ferric and chromic salts are entirely analogous in their action to aluminum salts, which is manifested by their conduct toward hide; likewise in their homomorphism with the aluminum salts, only they are not absorbed and fixed in such abundant amounts.

Tanning Experiments with Ferric Chloride.

Ferric chloride had been prepared from piano wire by dissolving in hydrochloric acid, oxidized with a few drops of nitric acid and evaporated to dryness in order to expel the excess of acid. In a dilute solution of this ferric chloride from 0.200 gr. of piano wire is placed 2.230 grs. dry, pure hide. After 48 hours, when the weight of solution amounted to 12.643 grs., an analysis

[7] "Apparently the aluminum salt combined with the hide is basic while an acid salt remains in solution." Berzelius, *Lehrbuch*, 9 372.

[8] Alum precipated with sugar of lead, as it is used in calico printing.

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on 6.433 grs. solution yielded 0.196 ferric oxide. The 0.200 gr. piano wire used:

Corresponds to 0.575
The 0.196 ferric oxide found afterward to 0.403 gr. ferric chloride
And therefore 0.172 gr. or 4¾ per cent

has been condensed on the hide. While aluminum salts, on account of their achromatism, form white leather, iron tanned leather possesses a brown to brownish yellow color, chrome tanned leather a grayish blue, natural color.

After the conduct of metallic salts it was of interest to study the behavior of indifferent materials on the hide. As is known, fats and similar bodies possess in marked degree the property of changing hide into leather, the question therefore is, what power does the hide possess to fix them.

Tanning Experiment with Stearic Acid.

A strip of hide weighing 1.062 grs. placed over night in a solution of 1.145 grs. stearic acid in 25.595 grs. of 80 per cent alcohol, then taken out and dried, had changed into a dazzingly white, tanned, fine grained leather; 3.512 grs. of the remaining solution gave 0.151 gr. stearic acid from which the total content calculated to 1.135 grs. Therefore there had been absorbed by the hide 1.145–1.135 = 0.010 gr. stearic acid, not quite one per cent.

In the second experiment 22.295 solution with 0.606 gr. stearic acid had been used for tanning 1.471 grs. hide with the same result. The residual solution yielded 0.535 gr. stearic in 22.295 grs. or 0.601 gr. in the entire solution; therefore 0.606-0.601 = 0.005 gr. stearic acid had gone over to the hide corresponding to ⅓ per cent.

Tanning Experiment with Oleic Acid

The alcoholic solution contained 1.201 grs. at the beginning, after tanning 1.132 grs. pure dry hide, 1.189 grs oleic acid; therefore there had been absorbed 1.201 – 1.189 = 0.012 gr. or 1 per cent.

Tanning Experiment with Train Oil.

2.181 grs. of washed hide were placed in a solution of 0.338 gr. train oil in ether. After tanning, the solution still contained

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0.328 train oil and therefore there had been absorbed 0.338 – 0.328 = 0.010 gr. train oil or ½ per cent.

Resins acted similarly to fats. A dilute solution of rosin changed the hide into a finished yellowish white leather.

Tanning Experiment with Rosin.

The solution consisted of 15.113 absolute alcohol and 1.505 rosin. After complete tanning of the 1.326 grs. pure dry hide placed in it, the residual solution yielded 0.154 gr. in 15.691 grs. of solution or in the whole a content of 1.549 grs. rosin.

In the second experiment the weight of the hide amounted to 2.653 grs., the content of the solution 0.293 gr. rosin. After tanning the solution still contained 0.043 gr. rosin in 4.166 grs. therefore in the whole 0.360 gr. rosin. In both experiments instead of an absorption, an increase of dissolved substance appears, in the first case of 0.044, in the other case of 0.039 gr. The reason for this anomaly was easily perceived. The hide used for the experiments was only washed in distilled water, not in alcohol, and therefore in the experiment it gave up to the alcohol some substance soluble in it. When in a third experiment, 2.831 grs. hide purified in water and alcohol was used then the case changed. The solution contained 0.510 gr. rosin before tanning, after tanning 19.732 grs. of the remaining solution, after evaporating to dryness, gave 0.415 gr. rosin. Calculated from that for the whole 0.495 gr. and there had been absorbed 0.510 – 0.495 = 0.015 gr. or ½ per cent of the hide.

In the fats and resins one, therefore, has bodies which on the one hand are entirely able to change hide into leather, however on the other hand they are not fixed by the hide from their solution, for what has been absorbed by the hide in the above experiments is barely beyond the error of observation.

The fixation of vegetable tannin is a problem of great interest but its purification is so difficult, and its variability is so great as to take all prospect of exactness from the experiment. However, in order to study in some degree the behavior of bodies of a similar nature, picric acid was selected, which as is known, has the property to tan in a marked degree. At the same time picric acid through its solubility in two available vehicles gave the opportunity to study the influence of the solvent.

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TANNING EXPERIMENT WITH PICRIC ACID.

Repeatedly recrystallized picric acid dissolved in alcohol served for tanning 1.871 grs. purified hide. The solution used amounted to 5.758 grs., 3.560 grs. of the same, first dried on the water bath, then in vacuo, gave 0.183 gr. picric acid. After complete tanning the solution still weighed 16.975 grs. and 13.618 grs. of the same gave 0.111 gr. picric acid; calculated for the picric acid content:

Before tanning	0.296 gr.
After tanning	0.138 gr.

Therefore the quantity fixed was 0.158 gr. or 8½ per cent of the hide.

When 0.867 gr. pure hide was placed in 14.528 grs. pure solution of picric acid in water, 6.964 grs. of which left 0.137 gr. picric acid, there still remained after tanning 13.756 grs. of solution, 11.585 grs. of which gave 0.075 gr. picric acid. Therefore the quantity of picric acid computed:

Before tanning	0.286 gr.
After tanning	0.089 gr.
Therefore there was fixed	0.197 gr. picric acid,

corresponding to 22¾ per cent of the hide.

There is also exhibited here proof that the hide fixes almost three times as much from an aqueous solution of picric acid (of 2 per cent content) as from an alcoholic solution of over twice the strength (4½ per cent content) while at the same time in the first case the hide amounts to over six times more than the picric acid and in the last case only three times more.

* * * * * * *

In all cases given there is produced each time a complete tannage. These experiments with balance and weights furnish the proof that in tanning the tanning material is by no means absorbed in a definite unchanged proportion, that this proportion depends on the concentration as well as on the nature of the solvent, and that finally, as with fats; a tannage can obtain without any fixing action of the hide on the tanning material, merely by that part of the solution, which after removal of the hide remains in the pores and dries there. Therefore, if the conception of a chemical combination of the tanning material with

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the hide can not be given further consideration, the question becomes so much the more acute, as to how the relation of one to the other shall be conceived. To this the following answer is given:

As remarked in the introduction, the animal corium consisting in its structure of free microscopic fibers, forms on drying an apparently homogeneous, fiberless, firm, translucent, horny mass; that the fibers agglutinate with great adhesion and without, or almost without, interspace, so that the dispersion of light, which lets the natural texture of the hide appear white, disappears and beams of light go through unbroken, as far as they penetrate at all. The fibers of the horny, dried hide adhere together so firmly and intimately in fact that it is not possible to separate them mechanically by staking and boarding, and give it that flexibility which is characteristic of leather. As highly as fat is suited to change hide into leather, so much the less indeed can a horny, dried hide be tanned by immersing in fat or by coating with it because it finds no interspace to effect penetration. In practical chamois tanning as is known, the train oil is coated on the wet hide, so that the fat follows directly after the water, which escapes by evaporation, and is drawn into the still opened interstices.

Now if the horny property of the natural hide, when in its untanned condition from the point of view of the tanner, is due to the adhering together of the fibers then it is to be expected that that means which prevents this adherence of the fibers on drying, and the converse, namely, produces leather-like properties, is good for tanning. In a wider sense the expert always as a rule claims hide as leather, as soon as its fibers in the dry state instead of adhering are free as in the wet condition. Tannage, that is the state in which the hide in the broader sense is called leather, is in fact not directly the product of a combination of the tanning material with the hide. This state chiefly depends not on the tanning material, but essentially on the condition of the hide; it is an entirely indirect product of the tanning material. A structure, originally not fibrous, as the bladder of an animal, can indeed be tanned, but the product will not be claimed by any leather merchant, saddler or cobbler as leather. The tanning materials have mainly no other importance than that they coat the fibers,

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in penetrating the pores of the hide. The most common and best, but not the only method of bringing this about is when the tanning material is precipitated on the fiber by surface attraction and is fixed like dyes on silk, wool or cotton. In other cases, where surface attraction is not sufficient to precipitate material from its solution, enveloping of the fibers occurs when the solution between the fibers is dried. Bodies closely related to the resins but soluble in water are precipitated by the fibers with the greatest avidity as tannic acid, picric acid, then the salts of the metallic oxides of the formula M_2O_3, further chromic acid, others weakly, still others like fat not at all. Certain tanning materials have the property of coating the fibers in such a manner, that adhering is entirely impossible and the hide appears on drying, without more ado, at once open and flexible (bark tannins and tannic acid mainly). With other tanning materials indeed, as alum, etc., adherence occurs; the hide to be sure, then appears dense and more horny after drying but the coherence of the fibers is very loose and the hide can be easily and completely converted into the condition of leather by staking and stretching.

The power of animal hide to insolubly precipitate on itself substances from solution, as is the case with tissues in general, depends on the tremendous increase of surface by the fibrous structure. The thickness of the connective tissue fibre in no case attains 0.01 line; with this thickness in a one line hide there would be upwards of 100 fibers and in one foot breadth 10,000, together 1,000,000 fibers occupy the space. In one foot length the surface of the fibre 0.01 line thick would be 0.000314 sq. ft. and the total surface of one sq. ft. of hide or 1,000,000 fibers 314 sq. ft. In reality it is far greater because the fibers are not only greater in number but are distributed in all directions by ramification.

If the pronounced opinion, according to which tanning is not a chemical but a purely physical process and leather in its broader conception is nothing more than hide in which, by some means, the fibers have been prevented from adhering on drying, if this opinion is the correct one, then the reverse must also be true and the hide itself without any tanning material must be capable of being changed into leather, if in some manner the adherence of the fibers on drying can be prevented. It is actually possible to demonstrate this by an *experimentum crucis*. If one considers

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that the connective tissue fibers are only able to adhere to one another when they are wet and permeated then the idea is conceived to bring the hide that is soaked with water into a solution which on the one hand displaces the water by endosmosis from the intersticial space, while on the other hand it removes the ability of the fibers to adhere together, consequently ether or alcohol.

If a purified piece of hide which has been dried superficially between absorbent paper or cloth without pressure is placed for several hours in ordinary alcohol and then, after it is drained, just as long in absolute alcohol or sulphuric ether, (it is necessary in order to promote exchange of solutions, to suspend the hide some distance from the bottom) then after removal and drying it possesses a dazzling white appearance and every property which any expert will require to pronounce it (tawed) leather. It is in fact a leather without any tanning matter, which, placed in water, immediately reverts to hide and on boiling to gelatin. If the alcohol used at the end contains water or the quantity used is so small that the immersed hide noticeably contains water, then after drying the hide does not appear as leather but it can be changed into such exactly like tawed hide, by staking (Stellen), with the greatest ease. Since a chemical compound requires at least two things then the converting of hide completely into leather by alcohol excludes considering tanning as the result of a chemical combination.

Concentrated salt solution also has the property of depriving animal tissues of their water content to such an extent that they no longer adhere together. Therefore it is possible to withdraw water from the hide with salt solution in the same way as with alcohol, the fibers are almost dessicated in the salt solution, so that they find no opportunity to adhere to one another in drying. In fact, if hide is soaked several hours in concentrated salt solution with excess of salt and then dried first between absorbent paper, and finally in the air, then it shows a decided, even if incomplete, tannage about like poorly made tawed leather.

What conclusions remain now to be drawn from the opinion that tanning is only a special case of dyeing, from the properties of leather, especially from its resistance to putrefaction, its flexibility as well as from the operation of dyeing?

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It is indeed required of leather in general that it shall resist putrefaction, still this is not to be taken literally but only relatively. In comparison with the hide it resists extraordinarily long but not completely; tawed leather the least, chamois and bark tanned leather the best. The tanning materials, as tannic acid, iron and aluminum salts are of themselves styptic and antiseptic, they form, at least the former and also fats, etc., a layer firmly adhering to and enveloping the hide fiber which coats the fiber almost like varnish, excludes the air and renders it less hygroscopic. Thus the apparently paradoxical fact, that a hide on the point of putrefying is made into leather in a decomposing infusion of tan liquor in which the putrefaction of the one immediately ends the decomposition of the other, is still in some degree obvious.

As in certain cases, as with bark liquors and gallotannic acid the tannage no longer deteriorates in water, even in water made alkaline, while the tannage in other cases (with alum, etc.) is broken up again by water. This is exactly the same condition which in dyeing is signified by fast and fugitive colors.

A question of preponderant interest is the time which is necessary for a definite tannage, the speed with which it takes place. In all cases noted of the experiments given, not days but only hours are necessary, often only one or one-half hour. It was found that the rapidity of tanning is greater in proportion to the difference in character of the liquids involved, that is, the liquid with which the hide is impregnated when inserted and the tanning liquid. The greater the difference is, in the nature of the liquid as well as in its density, they will diffuse into one another with so much the more energy. Therefore one can say at least so far as the above experiments extend, tanning proceeds more rapidly when diffusion of the liquids proceeds more rapidly. Hide impregnated with water, having alcohol, ether, syrupy ethereal tannic acid solution, or chromic acid solution (aqueous) as tanning liquid is converted in from one-half to one hour into leather.

Other influences also have an effect on the rapidity of tanning. Among these are the greater or lesser facility with which the tanning material is made insoluble by the surface attraction of

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the fiber and the nature of the vehicle in which the tanning material is dissolved. If this vehicle, like alcohol or salt solution, already has, inherently, the property to set the fiber in the condition of tannage, or to augment it, then the rapidity of tanning will be greatly increased.

It scarcely needs mention, that the thickness of the hide to a great degree determines the duration of tanning. Calf or lamb skins, which were used in the above investigations, naturally need less time than half-inch thick cattle hides. As is known, tanning with the tannin of oak bark is the one which takes by far the most time and therefore operating capital. For heavy sole leather up to three years are necessary in order to tan it completely and all methods to shorten the time are only successful at the cost of quality. In the nearly complete ignorance of the bark tannins in which we find ourselves, no point of view has been found from which to draw definite conclusion as to the cause.

If tanning is only a special case of dyeing, it cannot therefore be assumed that every coloration of the hide must also necessarily be claimed as a tannage. Dyed in a solution of indigo white and then exposed to the air, the hide is dyed a deep and full blue, in an infusion of nut shells deep black brown. In both cases (one must take great pains to remove the alkali of the indigo white by acidifying and washing out) there results after drying a firm horny mass, but no leather. Obviously these dyestuffs rather possess the property to glue the hide fibers together than to prevent them from adhering.

From these experiences with indigo and walnut shells it is urged, notwithstanding the opinion obtained on the essential character of leather and of tanning, to look over the field of present day dyeing practice, in order to see whether serviceable, practical methods of tanning are to be derived from it or if perhaps dyeing in its methods and practices can be turned to account with advantage for tanning.

Now it is a known experience in dyeing that a dyeing compound fastens itself on the fiber the most permanently and durably when it is precipitated directly on the fiber. Bodies were then selected which on the one hand can be fixed in this manner and on the other hand probably prevent as much as possible the adherence

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of the fibers and finally, while they satisfy the conditions of a rapid tannage, practically comply with the flexibility of the hide fiber, and at the same time resist the dissolving power of water as much as possible.

The tanning property of ferric oxide has been long known but up to the present, no one has obtained serviceable leather with it, partly because of the desire to use it on account of its color as a substitute for bark tanned leather and in competition with it, partly from defective knowledge of the conditions of leather formation. Ferric oxide and chromic oxide salts both, have in eminent degree the property to change hide into leather. In a solution of sulphuric, or better, hydrochloric acid, ferric oxide colors the hide a beautiful reddish brown; in a similar acid solution chromic oxide a beautiful bluish gray, but after drying it forms a thin, poor, cracky grained, often very brittle leather, more so if the tanning solution contains as little as possible, or no free acid. The iron leathers, as they have been usually produced until now are of this kind. For although free acid be absent, the acid reaction of the salt in question transforms the hide into a condition which only too easily hurts the product. A decided neutral or alkaline reaction transforms the hide into the swollen state which condition it retains during and after tanning. Leather from plumped hide, as sole leather, is thicker, more tense and firmer than from hides not plumped although ever so completely tanned. The acid reaction of the iron and chrome salts causes, with thin hides, a too stiff leather, especially subject to cracky grain. On the other hand if the solution of the chlorides be transformed gradually previous to tanning, with as much soda or caustic soda as it will endure without forming a permanent precipitate, then one has the double advantage that the oxide compound in this manner is precipitated more easily and more abundantly on the fiber; that the acid reaction on the hide (although not on litmus paper) is removed and finally that a quantity of salt corresponding to the addition of soda is formed. In other words a solution of ferric or chromic oxide prepared thus has the same relation to the plain chloride solution as the alum solution of the tanner has to aluminum chloride. By means of this solution the hides are tanned much more easily and with greater flexibility. They are in need of staking (Stellen), that is

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complete separation of the fibers by stretching and drawing before drying, like alum tanned leather. If instead of the aqueous, alcoholic solutions of the chlorides of aluminum, chromium and iron prepared in the same manner be taken, then tanning proceeds surprisingly easily and the leather no longer requires staking. All tawed leathers lose the tannage in water, and therefore they are only useful for objects which do not come in contact with moisture. In order to give them resistance to this element, an effort was made to convert the metallic oxides named into insoluble compounds on the fiber, at the same time retaining as much as possible the flexibility and softness of the hide fibers, promoting as much as possible rapidity of tanning and permanent fixation on the fibre. Of all compounds of metallic oxides in question there appears for this object none more suitable than those with the fatty acids, namely, the aluminum, ferric and chromic soaps. They are insoluble in water, in the dry condition more plastic than brittle, possess the color of the precipitated oxide and have the advantage that they can be produced by double decomposition from compounds soluble in water. Thereby the known principle based on the experience of practical dyeing comes into use, that a material can be fixed on the fiber the most permanently and stably when it is precipitated on the fiber from its constituents. The result corresponded in that respect to expectation.

For the purpose of preparing this new tannage, two baths are prepared, one with aqueous soap solution and the other with salt solutions prepared as above. For the soap bath, soft soap on account of its complete solubility is better, hard soap usually is only partly soluble in the cold, however as a rule soft soap injures the purity of the color of the leather in some degree, which is not the case with the usual soda soaps. Therefore if it is important to have a pure color, as with white alum leather, it is best to use a soft soap from caustic potash and pure fat (tallow, etc.) The soap baths must be dilute, that is, contain not more than $^1/_{20}$ to $^1/_{30}$ soap and when they are prepared from soda soaps, must be warmed to about 37° C. which is not necessary with soft soap. The solution of tanning salts shall likewise contain about $^1/_{20}$ of salt. The pelts are first placed in the salt solution, moved about in it briskly, taken out frequently to drain, placed in again, etc.,

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until they have absorbed properly and are impregnated, for which one to two days suffice. After they are drained for the last time they are placed in the soap solution for 1-2 days. Through residues of the salt solution clinging to the outside of the hide, which can never be completely removed before placing in the soap solution, a precipitate is always formed outside of the hide which without further detriment sinks to the bottom. After the tannage the hides are washed off and dried. If for this method of tanning alcoholic solutions of soap and tanning salts be used then the height of rapidity and completeness of tanning are attained; the leather so to speak, comes already finished from the liquor, soft and flexible. As one sees, this tannage with insoluble soap, in effect although by no means in principle, is similar to a mixture of tawing and chamois tanning. Leather tanned with alum and soap is white and possesses instead of the dry almost chalky feel of the surface of pure alum tanned leather a soft, more glossy and greasy feeling surface, as is also the case with iron and chrome leather. The color of these is the same as in tanning with the oxides alone, with iron reddish brown, with chrome grayish blue; if one tans with a liquor which contains a mixture of ferric and chromic salts, then a color is formed which by correct proportions can be made similar to that of bark tanned leather to the point of deception.

According to the same principle a kind of chamois leather can be produced; if a pelt is alternately treated with a solution of soap of strength designated above, and dilute acid, so that the fatty acids are precipitated on the fiber, only in this case one must take still more dilute solutions and the leather after tanning must be washed out well. It is best, first to place the hide in the acidified water and then in the soap solution, this to be repeated two to three times, until a test cut shows it to be tanned, then the hide is to be dried and after drying to be freed from adhering soap with the sponge.

Finally there is still to be mentioned, that an especially beautiful glazed leather as used for kid gloves can be produced if cleansed lamb or goat skin is tanned in a luke warm saturated alcoholic solution of stearic acid, for which the product of stearine manufacture appearing under this name can be used.

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Leather produced in this way is very soft and flexible, whiter than the usual kid glove leather and possesses an especially beautiful, natural glossy grain.

G. W. S.

THE COLOR MEASUREMENT OF VEGETABLE TANNING SOLUTIONS*

DR. BLACKADDER: The formal Committee report has already been published in the JOURNAL and I believe it might perhaps be advisable, and I think it is permissible, to make a few preliminary remarks and then just refer to some of the figures obtained which are contained in the report.

Of course the Committee working on the color measurement of vegetable tanning solutions should take cognizance of the skiver method and of the color machine method, but as this Committee's work was suggested by a paper published by myself and Mr. Garland on the possibility of devising a color machine operating on different principles than the present color machines, this was the phase of the subject which we studied.

As you probably all know, the Lovibond machine is the standard in Europe to-day and in this country we have no standard machine, but we have been trying, on account of trade relations with Europe, to use the Lovibond machine and the Lovibond machine has shown numerous disadvantages. Perhaps the most objectionable one is that when used in different localities or used by different operators, very varying results are obtained.

The Lovibond machine consists essentially of a dark box about 12 inches long, with the ends closed, and a hole in one end where you look in; at the other end two windows about one half inch or three quarters of an inch wide by an inch high, and they are spaced about three quarters of an inch apart. In front of one of these windows you put the colored solution, filtered according to the official method, which is supposed to be one half per cent solution with regard to the tannin material content, and in front of the other window you put the colored glasses—reds, yellows and blues, and you look into the hole at the near end and arrange your glasses so that the two windows look the same.

* Discussion of Committee Report read at Atlantic City, June 11, 1921. (See This JOUR., 16, 280).

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Now, apart from the difficulty of operating this machine, which is great, it seemed to me and some of the Committee that a color which was built up by a combination of glasses and then compared against the solution color was not a very satisfactory method of operation, because it is possible (and this has been the experience of numerous operators) to get more than one combination of the colored glasses which will look the same as the solution. We therefore looked around for some other method whereby we might examine, if possible, the amount of the different colors of the spectrum which was let through the solution. This of course could be done by spectro-photographs, but this would be out of the question for commercial laboratories. However, we did find a machine which fairly approached this method.

In this machine you have two windows at one end and the eye piece at the other end, but you put a screen in front of the eye piece, which only lets through the light from one part of the spectrum at a time, and then by suitable arrangement of the prisms and a shutter in front of one of the windows, you are able to measure the amount of light of that particular color which the solution passes. This machine is the Hess-Ives machine, which we set out to check up. On account of the special apparatus needed, the work was all done in one laboratory.

We took up three points. The first was the effect of the different illuminations, which is known to have a great effect upon the readings obtained in the Lovibond machine. We found in the Hess-Ives machine that the quality of the varying light from the regular Tungsten lamp running at a low voltage, which would give a yellowish light, to the daylight bulb, that is the blue bulb, which gives a very white light gave readings practically identical. The second point investigated was the difference with the various operators. Five men obtained close results. These two points were very encouraging; but when we came to trying to differentiate between different tanning solutions with this machine we found that we did not get a distinct difference in any one of our readings as you do in the Lovibond machine, where the addition of iron to the solution produced a rapid rise in the blue. We did find, however that the screens which the Hess-Ives machine uses to-day are not absolutely pure. We also found that when we examined our solutions in the

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spectroscope no solution, although we had a great amount of iron it it, let through any blue; that the color range was all between the red and the green. This seems to indicate that in our standard any use of a blue must be wrong.

We suggest that it is perfectly possible to obtain a series of color screens which will embrace just those parts of the spectrum that we want, and the best way to obtain these would be possibly to obtain spectro-photographs of typical extract solutions, and in that way the work should be carried further.

Now I wish to show you some figures which will illustrate some of the difficulties that we have with the Lovibond machine. I have here a couple of skivers which were made from the same extracts and a couple of readings made on the Lovibond machine. This extract was put through the analysis and the Lovibond reading was made. It read: Red 2.5; yellow 10.2; blue or black 0. The skiver was put through and came out in such a way that we thought that there must be something wrong with the Lovibond reading. The skiver test was put through again and it came out a fair match. We were satisfied that there ought to be a blue figure in the Lovibond reading of this extract, so we put in blues; we put in one blue which is an immense reading for a chestnut wood extract on the Lovibond scale, and we matched up the reds and yellows to go with that blue and we got a reading finally of 2.2 red, 8.9 yellow and 1.1 blue. These readings were checked by two men and a cautious man would not be able to differentiate between the first and second matches on the Lovibond machine.

PRESIDENT SMALL: The subject of "The Color Measurement of Vegetable Tanning Materials" by a tintometer has never interested the tanners of this country particularly. Color thus determined, however, has a fairly high ranking in the valuation of a tanning material by tanners abroad. For the benefit of the producers of extract in this country who do any foreign business, a study of the tintometer or other similar instrument by which colors may be measured seems of importance. It is to be hoped that there will be a sufficiently live interest in this subject so that the use of the Lovibond tintometer either may be thoroughly discredited,—that it may be shown that the results are wholly unreliable in estimating the color thrown on a hide by

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a particular tanning material,—or that the contrary may be shown to be true. If a color measurement by an instrument of some sort is demanded, and if another instrument is superior to the Lovibond, we should know it.

To the extent that this subject interests the producers of tanning materials here, who are looking for a foreign market, the work that our Association is doing on it should have their backing.

The subject is open for discussion and we shall be very glad to hear from any members who have any experience with the tintometer.

DR. BALDERSTON: I have had experience with the tintometer and believe that its indications have little value. The example which Dr. Blackadder gives of an extract which after treating was better than before and according to the tintometer was worse, may be duplicated over and over again. I suppose we have no better example than the fact that chestnut bark gives an extract much darker than chestnut wood but it makes a leather much lighter. The French extract makers throw away the bark because it makes the extract darker. As a matter of fact, it would improve the color of the leather made with extract if they would put the bark in.

I have just had another instance of it in the experiments described yesterday. The two barks alluded to had exactly the same relation. The ordinary *yezomatsu* gives a much lighter liquor than the red *yezomatsu,* but the red gave a much lighter leather. The color of the extract gives practically no indication of what kind of leather it is going to make. So that it seems to me that in a broad sense tintometer or spectrometer measurements of an extract give no dependable indication of what kind of leather the extract will make. In comparing chestnut wood extracts I admit that these tests have a value, because there is no doubt that the difference in color between different batches of chestnut extract is liable to be reflected in the leather, because those differences in color are due not to the innate character of the chestnut wood or the extract made from it but to some accident of manufacture. For any one kind of material, therefore, such examinations have a value which we need not deny, although broadly speaking the method is very misleading.

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MR. VEITCH: Mr. President, I agree with Dr. Blackadder that one of the things that should certainly be done here is a more extended photo-spectrometer study of the color of extracts, and we will be very glad to co-operate in this work; we have pretty good equipment of all sorts of spectrometers and instruments of various kinds, and I am sure we will be very glad to join the Committee work on this subject for another year.

MEASUREMENT OF THE IRON CONTAMINATION OF CHESTNUT EXTRACT*

By T. G. Greaves

The effect of iron on vegetable tanning materials is well known in a general way to every tanner and extract maker but on account of its importance a clearer concept seemed desirable. The following work was, therefore, undertaken to consider the progress of this contamination through the manufacturing process of chestnut extract and to express the effect in the increase of color which will serve as an indication of a loss in value.

A qualitative evidence of the affinity of chestnut wood for iron is the blue black stain left on the wood by the axe blade when a chestnut tree is cut down.

For such small quantities of iron the methods of drinking water analysis were found more suitable than methods which were intended for larger percentages. After burning off the organic matter from about 80 grams of original wood or 15 grams of extract, the ash was dissolved and made up to definite volume and suitable aliquots analyzed by the procedure given in Mason's Examination of Water. The method given for water analysis in Proctor's Leather Industries Laboratory Book would. however, be easier to use because it does not call for oxidation with permanganate.

For the sake of uniformity the iron is expressed throughout as a per cent of the units or weight of pure tannin, with the fresh wood taken as yielding eight per cent tannin. Eighty-eight parts of spent wood are taken as derived from one hunded parts of fresh wood and so are represented by eight parts of tannin. The iron in the leach water is based on the units it will contain after it goes through the leaches.

* Published by courtesy of the American Chemical Society. Paper read at the 62nd meeting, September 6 to 10, 1921.

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In order to get a sample of wood before and after the iron parts of the apparatus, the chipper, shredder and conveyors, were run empty until well cleared and a nine inch, fairly well seasoned stick was run through (after first being sampled by sawing a block from one end.) This block tested 0.0080 per cent iron. After going through the chipper and seven feet of an all iron drag, the chips tested 0.034 per cent or four times as much iron as before. After passing through six feet more of the all iron drag, a shredder, seventy-five feet of a drag with an iron floor and wooden paddles, and 30 feet of a screw conveyor, the chips landed on the floor of the leach house where the pile was stirred up by hand and two samples taken. One of these analyzed 0.145 per cent and the other 0.130 per cent, average 0.138 per cent or seventeen times as much iron as was originally in the wood.

The 0.026 per cent of iron added by the chipper and seven feet of drag is probably normal but the 0.104 per cent added by the rest of the equipment is not representative because the chips of the test stick spread over more of the iron floor of the long drag than when the chips are piled up as in normal operating. This latter figure is, therefore, disregarded and taken, in Table 1 by difference.

The work was continued by starting all around. Four representative sticks of from twenty-nine to fifty-five years growth tested 0.0080 per cent, 0.0021 per cent, 0.0039 per cent, and 0.0100 per cent; average 0.0060 per cent iron.

Four factory runs of untreated extract tested 0.030 per cent, 0.021 per cent, 0.025 per cent and 0.020 per cent; average 0.024 per cent iron.

Two samples of spent chips tested 0.0660 per cent and 0.0539 per cent; average 0.060 per cent iron.

A sample of water for the leaches going to the heater tested 0.0028 per cent and one coming from the heater tested 0.0032 per cent, but as another sample going to the heater tested 0.0032 per cent it is not determined whether or not an appreciable amount of iron is added by the heater. These samples were not filtered nor settled. A sample settled several weeks tested

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only 0.0004 per cent iron. No tests were made to find to what extent the iron of the suspended matter is dissolved by the extract and this is indicated below.

TABLE I.

Per cent iron (Fe) based on tannin units:	Per cent	
In untreated extract	0.024	
In spent wood	0.060	
Iron found in system	0.084	
This can be divided as follows:		
Originally in the wood	0.006	
Added by chipper and seven ft. drag	0.026	
Added by water	0.0004	(to 0.003 %)
Added by shredder and conveyors (By diff.)	0.0516	(to 0.049 %)
	0.084	

The striking proportion of iron that is held in the spent wood probably indicates that the larger particles of tannate of iron are collected and held in the ducts of the wood left empty by the removal of soluble matter while particles fine enough to be classed as a coloration pass on with the liquor.

For the expression of definite amounts of iron in color, the skiver is not available because it lacks numerical expression. A colorimeter test on the filtered solution is the only alternative. The Kerr modification of the Schmidt and Haensch colorimeter[1] is not as suitable for manufacturing control work as colorimeters using combinations of colored glasses because matching colors with solutions of the primary colors is tedious and because these solutions gradually fade, but for work such as this, solutions are more accurate because relative colors can be built up more mathematically with column lengths than with combinations of more or less arbitrarily marked glasses.

TABLE II.

THE EFFECT OF THE ADDITION OF IRON (Fe''') BASED ON TANNIN UNITS BY THE SCHMIDT & HAENSCH COLORIMETER AS MODIFIED BY G. A. KERR.

	Color Increase		
Iron added Per cent	Blue Per cent	Red Per cent	Yellow Per cent
0.0	—	—	—
0.025	33	13	3
0.050	63	26	5
0.075	89	38	5
0.100	127	52	8

[1] *J. A. L. C. A.*, Nov., 1914.

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Two lots of slightly decolorized extract which had ten per cent blue removed, analyzed 0.016 per cent and 0.016 per cent iron or 0.008 per cent less than the average "standard" extract. This checks Table II and shows that, in this case, the decolorization was due to the removal of iron. An extract of noticeably worse color than the "standard" grade (colorimeter reading was not made) analyzed 0.039 per cent iron or 0.015 per cent more iron than this grade.

In Table II the amounts of the color elements are determined by the column length of a solution built up to absorb and transmit the light supplied in the same proportion as the solution to be tested. A promising colorimeter, the Hess-Ives Tint Photometer, has recently come on the market and is being studied by a committee of the A. L. C. A.[2] which accomplishes the result in an easier way by the measurement of the per cent of each color element of the light supplied which is transmitted by the solution and a color screen, through one opening, as compared to the light transmitted by the screen alone through a similar opening. The latter is partly closed by a sliding shutter and the per cent opening required is read from a scale for each of three color screens.

Table III is the work of Dr. Blackadder,[3] refigured from per cent of 25 per cent extract to per cent of the tannin units, and from colorimeter readings to per cent loss of color transmitted as the solution increases in color.

TABLE III.

Iron Added Per cent of tannin units:	Per cent loss of color transmitted		
	Blue	Red	Green
0.01	14	6	13
0.02	36	8	15
0.04	43	18	27
0.06	50	26	35
0.08	64	37	45

As Dr. Blackadder has pointed out, determinations with the Hess-Ives, so far, cannot be considered as color analyses because the light attributed to each of the colors belongs in part to

[2] *J. A. L. C. A.*, March, 1920 and May, 1921.
[3] *J. A. L. C. A.*, May, 1921.

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one or both of the other colors, the screens not representing solid blocks of spectrum color or overlapping. This no doubt also applies to the dye solutions used in Table II which were originally selected for making color photography screens. Tables II and III are only applicable to the same color grades used in making the tables. These were good average extracts. A decolorized extract would show a greater per cent effect and one of bad color a smaller per cent effect.

It would be misleading to give in the table the equivalent in money loss due to the gain in color caused by definite amounts of iron because the methods of color testing have been so unsatisfactory that no standard has been recognized and no competitive value for good color has, so far, been established. In special cases, however, the value can be determined by measuring the color difference between standard and decolorized and applying the difference in price per unit to the amount of iron found, by the same colorimeter, to cause the same color difference. For example, several years ago, a firm was selling an extract with 10 per cent of blue color removed for 7½ cents a unit and the original for 7 cents a unit. Ten per cent blue color in Table II is equivalent to 0.008 per cent iron and this is here equivalent to $6^2/_3$ per cent of the price. Twenty per cent loss in value could then be written in this table, besides the 0.025 per cent iron increase.

Since the ultimate question is the effect on the color of leather that is tanned with an unfiltered solution and which absorbs the insoluble along with the soluble matter, while the colorimeter uses the solution after filtration, the readings would not give the full measure of the color if the tannate of iron were appreciably removed from the solution by filtration. Investigation of this point[4] has shown that skivers tanned with filtered and unfiltered chestnut extract solutions showed no appreciable difference in color.

Mobile, Alabama.

[4] *J. A. L. C. A.*, May, 1921.

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THE MICROSCOPE AS APPLIED IN THE MANUFACTURE OF LEATHER*

By Robin Bruce Croad and Fini G. A. Enna

I.

Two-Bath and One-Bath Chrome on Goat Skins.

The present work was undertaken in order to find an explanation of the differences in physical properties between goat skins tanned by the two-bath process and those obtained by the one-bath process.

The well-known glazed kid with its elasticity and almost cloth-like feel, which is the result of the two-bath process, has never, so far as we are aware, been produced by any one-bath process, though in both cases the tanning agent *may be* the same.

The difference must therefore be due to the production of basic chromic sulphate *in situ* as against immersion in a bath of basic chromic sulphate. Of any chemical difference between the two types of leather we are unaware, but it seemed probable, that the microscope might give some indication of the physical difference and the cause.

On seeking in literature for methods employed in the microscopical examination of leather, we only found one paper giving any detail whatsoever, namely that of Georges Abt, *Collegium* 1914, 527. We cannot but agree with Abt that the reason for the very limited use of the microscope in the leather industry is the lack of histological technique on the part of the Leather Trades' Chemist.

W. Moeller, in his articles (*Collegium* 1916, 544 and 550 to 557 inclusive), disagrees with Abt as to the lack of knowledge of microscopical technique, though the difficulties which Moeller mentions having met with are only the ordinary difficulties in the preparation of microscopical sections from pelt and leather. He gives no details of his own procedure, and thus no help was obtainable from this source.

Accordingly, we give full details as to the methods of obtaining sections, etc. We have drawn largely on the above mentioned work of Abt, and on that of Seymour-Jones, (*Collegium* London), 1915, (I, 15 et seq.)

*Presented before the Leather Division at the 62nd Meeting of the American Chemical Society, New York City, Sept. 6 to 10, 1921. Published by courtesy of American Chemical Society.

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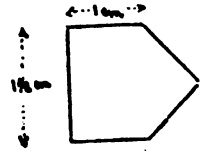
Experimental.

A dry-salted Madras goat skin was used. Sections were taken in the same direction throughout and in order to make certain of this, specimens of the pelt and leather were cut as shown in the diagram, the acute angle representing the *direction* in which the section was to be cut.



The method of preparing the pelt for making permanent sections without in any way altering the structure, was the chief difficulty. In all cases sections of the wet pelt or leather were taken and compared with the permanent section preparation. The method of obtaining sections from the wet pelt was as follows:—

A specimen shaped as above mentioned was cut and placed between two pieces of pith or cork and held firmly between the thumb and first finger, and the section cut with an ordinary razor ground flat on one side. With practice, sections of from 10-12 μ were easily obtained. The sections were floated in water, placed on a slide, examined under the microscope and those of suitable thickness immersed in a weak solution of magenta (one drop in 100 cc. of water), for fifteen minutes.

After trying various methods, the following processes were carried out:—

1. Fixing.
2. Dehydrating.
3. Embedding in wax.
4. Cutting.
5. Mounting.

1. Fixing. With the exception of certain sections mentioned below, we employed Abt's solution for fixing the sections. Abt's solution sonsists of

Saturated aqueous picric acid solution.....70 Parts
40 Per cent formaldehyde solution.....10 Parts
Glacial acetic acid ..... 1 Part

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The specimen of pelt was allowed to soak 24-48 hours in 20 cc. of the above solution. The pelt was coloured a strong yellow and though this is a disadvantage if subsequent staining is intended we found some form of staining necessary in showing up the internal structure of the pelt.[1]

2. Dehydrating. After fixing, the specimen was dehydrated as follows:—

A. Soaked in 30 cc. 50 per cent alcohol, 12 hours.
B. " " " " 75 " " " , 12 " .
C. " " " " absolute " , 24 " .

3. Embedding. In order to obtain a good penetration of the paraffin, the speciment was soaked in 30 cc. xylol for two hours.

For the actual embedding in wax we made small lead foil receptables, 4 cm sq. by ½ cm deep. These can be easily made as shown in the following sketches:—

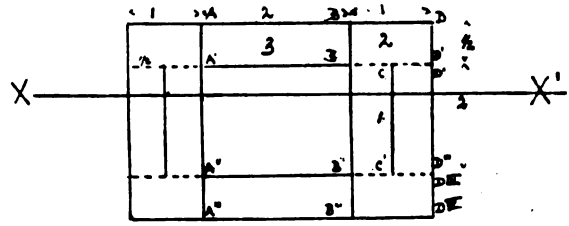

Fig. 2.
Fold along the continuous lines and cut along the dotted lines.

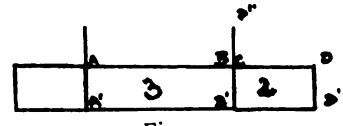

Fig. 3.
Cross section of Fig. 2 through XX′

Fold 2 at right angles to 3 along BB′ so that when 1 is folded along CC′, 2 comes between the fold. When completed, nip each corner to make joint tight.

The advantage of such receptacles is that the wax block can be easily removed without breaking when the embedding process is finished by simply tearing off the lead foil. A few drops of xylol were poured into the receptacle and then a thin layer of

[1]Seel and Sander, *Zeitschrift fur angewande Chemie* 1916, p. 333.

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molten paraffin wax, at 55-56° C. The specimen was then put in and completely covered with paraffin wax. The receptacles were placed in an air oven for 72 hours, the temperature being kept at 56-58° C. The receptacle was then allowed to cool for one hour and the lead foil removed from round the paraffin block; the specimens were found to be completely surrounded by wax.

4. Cutting. For this purpose, a Cathcart freezing microtome was used. A small quantity of molten paraffin wax was run on to the freezing table, and the block containing the specimen, cut to suitable size, placed, cutting edge up, into the molten wax. After fifteen minutes, or sooner if a little ether is blown through the chamber, the block was firmly set and sections of 0-10 μ were cut. For photograpical purposes, thinner sections are of little use, if structure is the object.

5. Mounting. Several sections of each specimen were cut, and the paraffin dissolved out by washing in six changes of xylol, 10 cc. for each wash. The sections were dried on filter paper between each washing; they were then placed on a glass slide, one drop of xylol placed on the section followed by two drops of Canada balsam. A cover glass was then allowed to fall from an angle on the Canada balsam globules, its own weight being allowed to spread the Canada balsam.

By this means air bubbles were avoided, and the structure of the section was not disturbed; this latter happens easily in the case of pelt specimens if any external pressure is applied, and the grain layer may separate from the flesh.

Exceptions to above Procedures. In the case of specimens taken from an acidified bichromate bath, they could not be treated with Abt's solution or alcohol owing to their reducing action; it was found that by soaking in three lots of xylol (30 cc.) over 24 hours and then embedding in wax, sections could be obtained in no way different from those cut between pith or cork.

Specimens of finished leather did not require fixing or dehydrating and were simply moistened with xylol and embedded in wax.

Photographing.

In photographing the sections the camera was fixed on the

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excellently devised apparatus of Seymour-Jones (*loc. cit.*). A Leitz microscope, No. 4 eye-piece and No. 3 objective were used. Ilford screened chromatic plates were used, and were exposed 45 to 55 seconds. To get the full detail, it is necessary to shut out the light from the mirror of the microscope almost entirely We find that day-light P. O. P. are less trouble and give more detail in printing.

Conclusions.

Sections from skins taken from the acidified bichromate and reducing baths and of a skin from a one-bath tannage seem to us to explain the different properties and their causes in glazed kid. The osmotic pressure of the bichromate in the acified bath caused a shrinkage and crowding together of the fibres; the cells of these, therefore, are under considerable strain so that when the pelt is introduced into the reducing or second bath, not only do we have the disruptive force of the reducing action, but immediately preceding this the decrease of the internal strain on the cells of the fibre, the sum total of both actions being to destroy the natural position of the fibres and to break up the hyaline layer, as was shown in a section prepared from the second bath.

In the one-bath tannage, however, there is only a slight osmotic action. Such action being to contract the cells, which become tanned in this condition, would therefore tend to give a tighter leather than otherwise. The fibers are still in a normal condition, with the hyaline layer markedly intact.

Every chemist is aware of the violence of the reduction of acidified bichromate, even in dilute solutions, and in the two-bath chrome tannage this reduction takes place within the fibres, the reagents being in an ionic condition, so that the violence of the reaction must bring about a disruption of the fibre. In the one-bath process the ionisation effect can only be small due to the semi-colloidal condition of the basic chromic sulphate, so that one would not expect any alteration in the structure, but any such alteration would tend to give a tighter leather.

If the above assumptions are correct, it would seem that to prepare glazed kid with its characteristic properties by a one-bath process is almose hopeless. This is confirmed by practical experience.

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An additional cause, though of much less probability, of disruption within the skin is the liberation of excessive SO_2; this recalls the peroxide reduction of bichromated skins whereby oxygen is claimed to be liberated *within* the leather during tannage. The importance of this fact is, to our minds, very doubtful. We intended to carry out similar experiments on calf skins, but time did not permit and we must reserve this part of our work till a later date.

We desire to acknowledge the generous support accorded us by Mr. Ernst Enna, and we tender our thanks to the directors of Messrs. Harold M. McArthur & Co., Ltd., Aintree, Liverpool, who kindly put at our disposal the facilities without which we should have been unable to carry out the practical experiments.

As to our methods and conclusions, we need hardly add that we would gladly welcome criticisms of both and we also hope to receive some helpful suggestions as to improvements in our treatment of this far to little known field of investigation.

Liverpool, August, 1921.

ABSTRACTS

Water in Relation to Dyeing. By J. MacGregor. *Col. Tr. Jour.*, 9, 43 (1920). The author treats of the properties of water, and the source and nature of industrial water in some detail which is followed by some effects of water in dyeing. The first requisite of a water from the dyer's standpoint is that it should be clear and free from sediment, as suspended impurities will be deposited on the goods giving rise to streaks and stains. Water having an appreciable color is unfit unless it is in the production of very dark shades. Water containing dissolved organic matter is objectionable because it is inclined to take up iron in its flow through pipes and storage tanks. In dyebaths prepared with basic dyestuffs any marked degree of temporary hardness may result in the precipitation of the color which takes the form of a curdy mass that possesses no dyeing properties and adheres to the goods as a sticky mass. The only effect that may be noticed sometimes in the use of very hard water in the dyeing of acid colors will be the dulling of certain bright shades. Substantive or direct cotton dyes as a rule are precipitated by lime and magnesia. When water containing these are employed for this type of dyestuff it must be properly corrected. The use of acid for this purpose is not available as in the case of basic dyes, owing to the fact that the dyebath must be neutral or alkaline. The most satisfactory way to correct it is by adding a small quantity of soda ash and boiling. Sulfur

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dyes are also precipitated by hard water and it must be corrected as for substantive dyes, Eosine and Rhodamine colors very readily form insoluble lakes in hard water. These dyes are especially valuable because of their delicate bright pink shades which are apt to be much dulled if the dye-bath is prepared with hard water. In the use of mordant color, and more particularly the alizarines the effect of hard water is frequently more beneficial than otherwise. In fact under certain conditions it becomes necessary to add lime salts to the bath to get the desired result. The presence of iron salts has a "saddening" effect on the color and water containing iron is to be avoided unless it is desired to sadden the color to obtain a desired effect.

In the case of dyeing Alizarine Blue, also Alizarine Blue S, the use of hard water is to be avoided as lime and magnesium salts precipitate insoluble color lakes. Hard water for this purpose can be corrected with acetic acid.

Nitrocellulose and Its Solution as Applied to the Manufacture of Artificial Leather. By W. K. Tucker. *J. I.* and *E. C.*, 13, 623 (1921). The point of first importance in the use of nitrocellulose is viscosity. It is determined by preparing a standard solution of 16 ozs. of nitro-cotton to one gallon of solvent (70 per cent ethyl acetate and 30 per cent benzene) and noting the time taken for a steel ball, $^{5}/_{16}$ inch in diameter to drop through a 10 inch column of this solution at 25° C. The addition of non-solvents such as benzene always increases the viscosity of nitrocellulose, hence the low viscosity cotton is logically the grade most suitable since it will allow the addition of a large amount of cheap non-solvent. Varying degrees of nitration affect the solubility of nitrocellulose in the commonly used solvents. The nitrogen content averages about 12 per cent with a range of from 11.5 to 13 per cent. Ash tests are always made although it is of minor importance.

Two solvents for nitrocellulose are very generally used in practice for the manufacture of artificial leather. These are acetone oils and ethyl acetate. The non-solvents are usually benzene and benzine.

The Vacuum Extraction of Tanning Materials. By A. Harvey. *Lea. World*, 13, 405 (1921). Up to the present time extraction of tanning materials has been conducted either by the open leach or pressure autoclave treatment. A method of extraction in vacuum has been put in operation in South Africa for wattle bark extract known as the "Nance" process that promises good results. The plant consists of a battery of five autoclaves. Chopped green bark is put in the autoclaves and vacuum produced in each by means of an ejector pump. Each autoclave receives five washings with water and the maximum temperature reached during the leaching is not higher than 21° to 22° C. at which temperature ebullition takes place. The leaching is of short duration and passage of the five waters through the five autoclaves can be accomplished in one day. The leach liquor which is 66° Bark. is run off into settling tanks

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after which it is evaporated in a Kestner triple effect and then a Kestner finisher to produce a solid extract. Analysis of the first extract made was as follows:—tannin—72 per cent; non-tannin—12.8 per cent; insoluble—0.6 per cent; moisture—14.6 per cent. The writer claims that this process is producing about 1 ton of extract from 3½ tons of the green bark.

The Determination of Alkaline Sulphides in Lime Liquors. By F. G. A. Enna. *J. S. L. T. C.*, 5, 131 (1921). Following a discussion of the reactions between a mixture of lime and sodium sulphide and their resulting products, a method is given for determining available sulphide in lime liquors using CO_2 to decompose the alkaline sulphide. The apparatus consists of a CO_2 generator and a wash bottle for the CO_2 gas containing sodium carbonate solution; a distillation flask containing a three hole stopper, which takes a separatory funnel, a tube which conveys the CO_2 from the generator to the bottom of the flask and an outlet tube which delivers the gas into a receiving vessel containing copper acetate solution.

In the receiver 15 cc. of a copper acetate solution (20 grams of pure copper acetate in 500 cc. water with 2-3 cc. of glacial acetic acid) is diluted to 150 cc. with boiling distilled water. After filling the apparatus with CO_2 the supply is cut off and 25-50 cc. of the lime liquor added through the separatory funnel and washed down with boiled distilled water. The liquid in the flask containing the lime liquor is heated until ebullition starts when CO_2 is again passed through at a fairly fast rate for about 20 minutes, when the liquor will be evaporated nearly to dryness. The flame is then removed and, after a few minutes, the receiver is removed, the contents brought to a boil, the cupric sulphide filtered off and washed well. The solution is cooled and titrated with N/10 sodium thiosulphate after adding 10 cc. of sulphuric acid (1:2) and 10 cc. of a 25 per cent KI solution using starch as indicator. Sodium sulphide is analyzed by this method by dissolving 5 grams in 500 cc. and using 10 cc. of this solution together with 25 cc. lime water for the determination.

The Manufacture of Single-Bath Chrome Liquors. By A. Harve *Lea. World.*, 13, 403. 502, 587 and 671 (1921). Methods are given and discussed for producing single-bath chrome liquors:—(1) By rendering chrome alum basic with soda ash and soda crystals which is also applicable to other chromic salts; as, the sulfate, chloride, etc. (2) By the reduction of bichromate with (a) organic materials; as, glucose, glycerine and waste materials (b) inorganic materials as thiosulfate, sulfur dioxide, sodium sulfite and bisulfite and iron salts.

Notes on Fur Dyeing. By W. F. A. Ermen. *J. Soc. Dye.* and *Col.*, 37, 168 (1921). The use of organic bodies, not in themselves dyestuffs, was first adumbrated by Erdmann's patent in 1888, for the application of paraphenylene diamine as a hair dye, in place of the very poisonous salts of lead or silver then in use for that purpose. He proposed to apply a solu-

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tion of paraphenylene diamine made alkaline with caustic soda. It was soon found that this solution was extremely irritating to the scalp, and the use of the sulphonic acid of phenylene diamine was patented, together with the addition of sodium sulphite.

In 1894, *p*-methyl amido phenol sulphate (metol) and diamido phenol sulphate (amidol) were patented as fur dyes, and placed on the market as "Ursols" by the Berlin Anilin Company.

In rapid succession followed patents for the use as fur dyes of substituted diamines, such as dimethyl para-phenylene diamine, amido phenol and its derivatives, and the methyl and ethyl ethers of amidol. Subsequently it was also proposed to use various diphenylamine derivatives containing amido or hydroxyl groups in the para positions. All these bodies are in themselves colourless, but possess the property of forming intensely coloured brown or black insoluble oxidation products, in presence of a mild alkaline oxidising agent. The constitution of the final oxidation products does not appear to have been much studied.

The method of application of these bodies to furs is as follows—

The fur is wetted out in a weak cold solution of caustic soda (3° Tw.) sodium carbonate, (9° Tw.), or ammonia, and then mordanted in a cold bath for about twelve hours, containing 0.5 per cent of acetic acid, together with 0.5 per cent of either sodium bichromate, ferrous sulphate, or copper sulphate, or a mixture of these.

After mordanting, the fur is well washed in cold water and may then be either dried up and kept till required, or entered at once into the dyebath. This contains from 0.1 per cent to 0.5 per cent of the dyestuff. The fur is turned in this for some time, after which it is taken out and the bath made slightly alkaline with ammonia. After being worked in this for about half an hour, hydrogen peroxide (12 vol.) is added, at the rate of from 20 cc. to 80 cc. per litre of dyebath, and the fur allowed to lie in this overnight, when the colour will be found fully developed.

Patterns of dyed furs were shown to illustrate the shades that could be obtained by this process, the mordants used being—Bichromate, bichromate and copper sulphate, ferrous sulphate, ferrous sulphate and copper sulphate.

The shades produced were—

p-Phenylene diamine	Deep brown black.
Dimethyl *p*-phenylene diamine	Bluish-black.
p-Amidophenol and cresol	Reddish-brown.
o-Amido phenol	Yellow-brown.
Amidol	Dark brown.
Diamido anisol	Grey.
Diamido anisol and phenylene diamine	Blue-black.
Diphenylamine derivatives	Bluish-blacks.

Insoluble Hide Powder. By G. Baldracco and S. Camilla. *Le Cuir*, 10, 354-5 (1921). While agreeing with Zeuthen (*Coll.*, 612, 181-3, 1921; Abst., This Jour., 16, 516, 1921) that a chromed, dried hide powder ready for use without washing is desirable, it is pointed out that Zeuthen must have

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overlooked previous work by the authors in which it is shown that the filter method should be abandoned and that such thorough washing as Zeuthen gives before dehydrating with alcohol removes all the acid from the hide powder. This acidity is necessary for the complete absorption of the slightly soluble, colloidal tanning materials present, *e. g.*, the phlobaphenes. The authors recommend that a commission of leather chemists study the question of tannin analysis and devise a rational method using a lightly chromed hide powder ready for use.

R. W. F.

Use of Formic Acid in the Tannery. ANON. *Le Cuir*, **10**, 360-1 (1921). A comparison of sodium bisulphite and formic acid for deliming will show that while the former is very good, the latter is better and nearly ideal. Sulphite contains sulphates, which are increased by oxidation, and consequently precipitates difficulty soluble calcium sulphate. It may also, although seldom, cause an undesirable formation of colloidal sulphur in the hide. Sulphite must be used in rather strong solutions and while eight times cheaper than formic acid, ten times more of it is required, and it thus proves more expensive in the end, especially as deliming with sulphite must be done by drumming whereas with formic acid the suspension method can be used.

R. W. F.

Comparison of Different Methods for Lime Liquor Analysis. BY O. SINGER. *Le Cuir*, **10**, 356-60 (1921). Considerable analytical data are given in a study of various methods for the complete analysis of lime liquors. A comparison of the determination of free ammonia by the methods of Schloessing, Procter and Thompson-Suzuki shows that the three procedures give nearly the same results. The last is the most rapid and practical method. With old limes Schloessing's gives the highest results, probably because of the formation of ammonia through bacterial action during the long time of standing, 72 hours. These methods give, however, only an approximate value as the lime and magnesium form complex salts with the ammonia which is not determined. In the determination of total nitrogen by the Kjeldhal method, acidification before evaporation or digestion gives the most accurate results, as otherwise during evaporation to remove the free ammonia, the lime converts a part of the hide substance into ammonia or volatile amines. The determination of sulphides by the zinc sulphate method, while difficult, has not been replaced by a better method. Attempts to determine sulphides by distillation with sulphuric acid were not successful because of interference of sulphites. Figures are given on the determination of albumins (Schroeder), peptones (Hallopeau), carbonated fixed residue and ash, free and combined lime. The data on alkalinity are given with the full text of the report on the subject by the committee on limeyard control. [*J. S. L. T. C.*, 4,114, 1920. This JOUR. 15, 620 (1920).]

R. W. F.

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The Separate Utilization of Rabbit Fur and Skin. ANON. *Le Cuir*, 10, 393-5 (1921). Skins of poor quality as to fur are used for felt by the hat industry and some means to utilize separately the fur and skin has been eagerly sought. There are three processes which have appeared plausible but are not extensively used. The first consists of painting the flesh side with lime and sulphide and piling flesh to flesh for a few hours. The objection to this method is that the roots of the hairs retain some of the sulphide so that it must be washed out and moreover the hair can only be processed with the carroting agent (mercury and nitric acid) in bulk which impairs its sale. In the second method the dampened skin is placed over a wooden support the shape of a paraboloidal dome and mechanically sheared. The objection of processing the fur in bulk also applies to this method. The third procedure might be called the ice or freezing method and has been applied in the manufacture of artificial garments. It is, however, not satisfactory for such purposes as a rubberized fabric must be used for holding the fur, thus producing an impermeable and consequently non-hygienic wrap. It would seem that the procedure could be modified for obtaining fur for hats. The softened skin is put on to a frame and placed in a tank of water, which is in turn put into a freezing brine of 5° C. to 15° C. When the water freezes, the cake of ice containing the skin is removed, the ice broken off down to the pelt, a little warm water put on to the flesh side to melt the ice in the pelt and the latter then quickly pulled off leaving the hair set in the ice. To facilitate the removal of the skin the flesh can be painted with sulphide before freezing. After removing the skin the roots of the hair must be washed. If it is desired the hairs are then set in a fabric with rubber but for hat fur it is simply necessary to lay the cake of ice on a cloth and let melt, the hairs being thus distributed over the cloth very much as on the original skin and can be properly processed. It is certain that rabbit skins can be used in the Morocco trade, maybe even for foot wear as the skins while having certain grain defects are of very good quality. It is difficult to change the routine of the felt cutters especially as the hat makers are so insistent upon having the hair or fur in the same position as when on the animals' backs and actually dread purchasing mixed hair. When the hat maker prepares the hair himself he will certainly find a way to save the skins.

R. W. F.

The Recovery of Acetic Acid During Evaporation of Tannin Extracts. *Le Cuir*, 10, 392-3 (1921). Dr. Jedlicka, chemical engineer for an oak extract plant in Slavonia, in a letter to Dr. Schell states that neutralization of acetic acid vapors from the evaporators has been practiced by them for some time with the sole object of protecting the installation, condensers and pumps, from the action of the acid vapors. The process was successful enough in this respect, even though the equipment, which consisted of large copper saturators converted from evaporators of a sugar factory, was relatively costly. For some years the crude acetate of lime thus obtained (about 7° Bé) was disposed of to a neighboring wood

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distillation plant and consequently all expense of subsequent handling was avoided. But since 1917 through the compulsory shutting down of the wood distillation works the acetate of lime has been handled, *e. g.*, filtered, evaporated, dried, and ground, by the extract plant, and the cost of operation so increased in proportion to the small quantity of product that it is no longer a matter of economy. About 250 kgs. of acetate of lime (80 per cent) are obtained per day from 90 tons of oak wood. The product is of good enough quality and by an additional purification could be substituted for sodium acetate in textile printing. A snow white product has been obtained by a very simple treatment. The conditions for recovery are similar in the manufacture of chestnut wood extract, but the author has had no experience with quebracho. One weakness of the procedure is foaming over into the lime solution even with a trap, so that tannin is lost and calcium tannate formed, the separation of which complicates matters. It is concluded that the process of recovery is not profitable. It is not patented either for recovery of acetic acid or acetate of lime.

R. W. F.

A New Iron Salt. By O. Röhm. *Coll.*, 614, 282-4 (1921). Ferric chloride is the most suitable salt for tanning but it absorbs water and hydrolyses so readily that it should only be shipped in glass or earthenware containers. Ferric sulfate is too difficultly soluble in water. By oxidizing a concentrated solution of iron vitriol with chlorine and allowing the water to evaporate crystals of ferric sulfate chloride ($FeSO_4Cl$ $6H_2O$) were obtained. This salt was very stable, was not hygroscopic, and gave better leather than ferric chloride. That it was neither a mixture of the sulfate and chloride nor a double salt was shown by the facts that it was completely soluble in alcohol and water while ferric sulfate is not, that it did not dissolve in ether with the separation of the chloride, that it was not hygroscopic and that the residue from a portion of the salt which had been partially dissolved in alcohol had the same composition as the salt in solution. One hundred parts of water at 20° C. dissolve 209 parts and 100 parts of 95 per cent alcohol dissolve 103 parts of this salt. The salt can also be formed by heating ferric chloride with either ferrous sulfate or sulfuric acid. The preparation and use of this salt is protected by patents. Jackson and Hou, This Jour. **16**, 144 (1921) oxidized ferrous sulfate with chlorine but did not prepare the solid salt.

I. D. C.

The Physiological Significance of Tannic Acid. By F. Czapek. *Coll.*, **613**, 227-32 (1921). Tannin is considered by many as a waste product while others maintain that it has an important part in life processes. Light causes an increase in the quantity of tannin. Büsgen (Beobacht. über die Verh. des Gerbstoffes Jena, 1889) found that leaves in the sun contained 3–4 times as much tannin as those in the shade. Cavozza Zeit. wiss. Mikr., 26, 59 (1909), found a maximum amount of tannin at 6 P. M. and a minimum at dawn and in evergreen leaves a minimum in

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March and a maximum in September. Tannin is, according to Sachs (Keimung der Schminkbohne Sitz. ber. Wein AK., (1859),) formed in tannin free seeds during germination. Kraus (Sitz. ber. Nat. Ges. Halle, 5, Nov., 1884) found that colored leaves contained more tannin than green ones, that falling leaves contained as much tannin as leaves at the height of vegetation, and that the heart wood of trees contained much more tannin than the sap wood. There is a relation between tannins and carbohydrates and probably between tannins and albumins. Kraus found there was a decrease in the tannin when the carbohydrate assimilation was stopped, and Büsgen was able to increase the tannin in leaves kept in the dark by adding sugar. Möller (Ber. bot. Ges., 6, p. 66 (1888), thinks that tannins, since they are glucosides, act as sugar carriers. Tannins also unite with alkalies and alcohols and might act as oxygen carriers. There is a relation between tannin and the formation of coloring matter in plant cells, especially the formation of anthrocyanid color, but the exact relation is not known. The accumulation of tannin in the outside of living and dead tissues protects the plants from animals and decomposition by bacteria, etc. Plants can however live without tannin for Pfeffer (Unters. a. d. botan. Inst. Tübingen, II, 197 (1886)) could precipitate the tannin from certain cells with methyleneblue without injuring the cells and Aschoff (Landw. Jahrb. 19, 127 1890), found that no tannin was formed in *Phaseolus* when grown in a chloride free medium. There is little justification for the view that tannin furnishes the energy for germination (albo-nouv. Giorn. Bot. Ital., II, 52 (1904)) or that the tannin of *Gunnera* is a respiratory material (Arnhold-Dissert. Kiel 1911.) or for the division of tannins into classes such as the division into systematic and non-systematic by Nickel (Bot. Zentr. 45, 394 (1891)) physiological and pathological by Wagner (Jour. pract. Chem. 99, 294 (1886)) or fixed and moving by Kraus.

I. D. C.

The Analogies Between Research on Leather and Textile Material. By W. Moeller. *Coll.* **165**, 314-19 (1921). The fibers in leather are in most cases woven together very irregularly but the direction of the fibers in some kinds of skins, *e. g.*, those of amphibia and fishes, is very similar to that in artificially woven materials. Rollet and also Knapp showed that the microscopic structure of skin was made more prominent by tanning, however, Moeller found that the smallest fiber elements changed their relative position during tanning and that this change could be detected optically and physically. Nägeli's micellar hypothesis has been found very useful in the study of the elementary structure of leather fibers. The micells may be woven into the fibers parallel to or spirally around the long axis and the effect of tannins on the relative positions of the micells causes the different physical characteristics of the various tannages. Advances in the chemistry of cellulose should be made use of by leather chemists since the two fields are closely related. Comparison of Heuser's work on cellulose and Moeller's work on hide substance shows that the processes of oxidation, hydrolytic decomposition, and acid and alkaline

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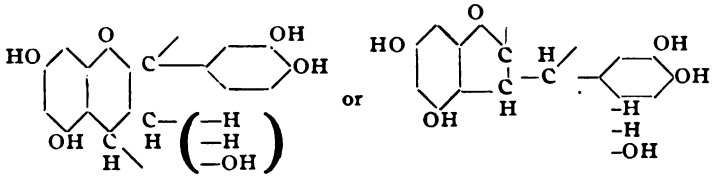
hydrolysis for the two materials are identical. Roentgen rays will doubtless prove very useful in the study of fiber structure, especially with the method of Polanyi, in which pressure is applied to the fibers until fusion begins, so that the particles can arrange themselves systematically around the main axis. I. D. C.

Contribution to the Knowledge of Catechin. By K. Freudenberg, *Coll.* **614**, 284-8 (1921). A methylated decomposition product of catechin discovered by Kostanecki in Indian acacia has been found by Freudenberg to be pentamethoxy-$\alpha\gamma$-diphenylpropane. Catechin therefore may have either of the following structures:



Catechin therefore has the same arrangement of carbon atoms as the flavon dyes and anthocyanidin and is very similar to quercitin and cyanidin. These substances usually have phloroglucin as one of the benzene rings while the other ring varies from benzene to pyrogallol. Many methyl-ethers and glucosides of various kinds also occur. Perkin has found a catechin in *uncaria gambier* which is very similar to Kostanecki's aca-catechin. These give the same diphenylpropane derivative and this derivative has been compared with and proved to be identical with the synthetic propane compound by taking the melting point of mixtures, study of the elementary composition and also by extensive crystallographic measurements. Measurement of the optical activity in aqueous acetone solutions showed that the gambier catechin was dextrorotary and aca-catechin laevorotary. The rotation of the aca is slightly less than that of the gambier catechin but this is probably due to the fact that the gambier is very easily extracted and therefore not changed during this process, while the aca-catechin is difficult to extract and is partially changed during extraction to the racemic compound. The mother liquor from partially racemized *d*-catechin was found to contain a new non-crystallizing catechin like material. The following pure materials have been prepared: *d*-catechin from gambier, racemic catechin from a mixture of gambier and aca-catechin and a new racemic catechin made by rearrangement from the above racemic catechin. The author now thinks he has the necessary foundation for synthetical investigation of the constitution of catechin.
I. D. C.

The Relation Between Hydrolysis and Adsorption III. By W. Moeller. *Ledertechn Rund.*, 13, 105 and 113 (1921).

A reply to the criticisms of Gerngross. [*Berichte uber die gesamte Physiologie and uber die experimentalle Pharmakologie*, 5, 326 (1921)] and of Kubelka [*Coll.*, 135, 1921; Abst., This Jour. **16**, 590 (1921)] of the author's work appearing under this title. G. W. S.

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Process for Tanning by Means of Unsaturated Fatty Acid. By W. FAHRION. *Ledertechn. Rund.*, 13, 126 (1921). Ger. Pat. 338,476. The fatty acids are prepared from train oils or linseed oil by saponifying acidulating and dissolving the fatty acids in 90 per cent alcohol. The alcoholic solution is cooled at 0°-5° for 8 days and then filtered from the solid acids. The unsaturated fatty acids in the alcoholic solution can be used in this medium after diluting to 10 parts of alcohol for 1 part of liquid fatty acids or the alcohol can be evaporated and the liquid fatty acids used in the usual manner. The by-products of this operation—glycerine and solid fatty acids—can find a ready market. The hide or skin to be tanned is prepared in the usual manner and sufficient of the fatty acids are used in tanning to give a complete tannage, but not enough in excess to make degreasing necessary. G. W. S.

The "Sulfolysis" of Hide. By W. MOELLER. *Ledertechn. Rund.*, 13, 121 (1921). A reply to the criticism of Immerheiser. [Abst. This JOUR., 16, 520 (1921)] of the author's paper concerning the hydrolysing action of neradol and ordoval on hide substance [see This JOUR. 16, 167 (1921).] Ordoval G and 2G have a high ash content which nearly corresponds to the non-tannins by the hide powder method of analysis and which consists almost entirely of sodium sulfate. A series of experiments were conducted with solutions of sodium sulfate and hide powder in the same manner as reported previously for the solutions of synthetic tannins. 1, 3, 5, 10 and 15 per cent solutions of sodium sulfate were used with 4.4 grams of hide powder and stood for periods of 8 days, 14 days and 3 weeks. The amount of hide substance found in solution increased with increase in time for each concentration. The 1 per cent and 3 per cent solutions give about 25 per cent of the hide in solution after 8 days and about 40.5 per cent after 3 weeks. With increasing concentration of sodium sulfate the amount of hide in solution decreases until the 15 per cent solution which shows a normal amount. From which the author claims the hydrolizing effect of the free sulfonic acids is augmented in practice by that of sodium sulfate. He conjectures that sodium bisulfate exists in conjunction with the normal salt in such extracts and that the hydrolizing effect of the former will be much greater than that of the latter.

G. W. S.

PATENT

Synthetic Resins; Synthetic Tanning-Agents. British Patent 163,679. M. MELAMID. Frieburg, Baden, Germany. Nov. 26, 1920. Cresols are mixed with an acid and a catalyst—in an example sulphuric acid with mercury and ferric salts—and acetylene is passed in: the reaction product is dissolved in benzene, freed from acid and salts by washing, and distilled *in vacuo*; cresols and benzene distil off up to 100° C., followed by a liquid product up to 200° C., the residue being a resinous solid soluble in alcohol or benzene. The liquid distilling up to 200° C. is converted into a tanning-agent by sulphonation.

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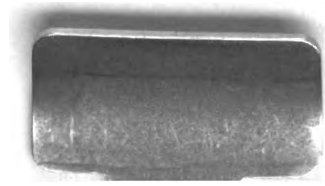

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